Development and Performance Evaluations of HfO_2-Si and Rare Earth-Si Based Environmental Barrier Bond Coat Systems for SiC/SiC Ceramic Matrix Composites

Dongming Zhu

Materials and Structures Division
NASA John H. Glenn Research Center
Cleveland, Ohio 44135

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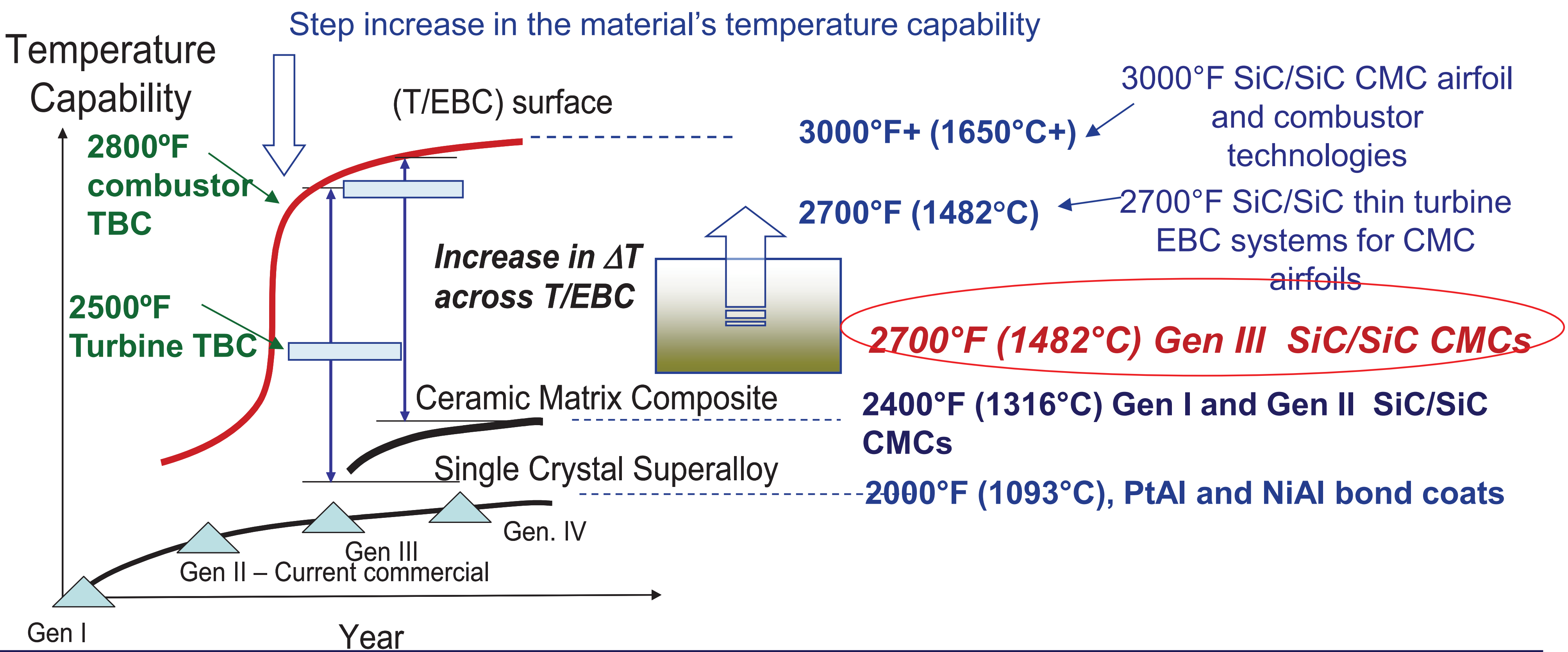
NASA EBC and CMC System Development

– **Emphasize temperature capability, performance and *long-term* durability**
- Highly loaded EBC-CMCs
- 2700-3000°F (1482-1650°C) turbine and CMC combustor coatings
- 2700°F (1482°C) EBC bond coat technology for supporting next generation
  - Recession: <5 mg/cm^2 per 1000 h
  - Coating and component strength requirements: 15-30 ksi, or 100- 207 MPa



Outline

- **Environmental barrier coating (EBC) system development: needs and challenges**

- **Advanced bond coat development approaches, NASA HfO_2-Si bond coat systems**
  - Focused on oxidation resistance, high temperature strength, toughness and creep properties

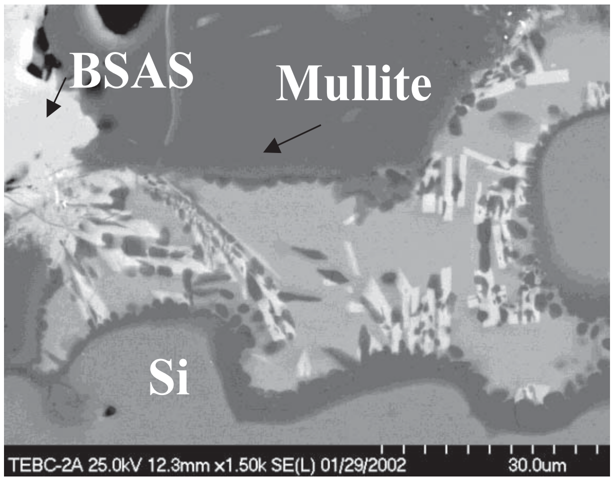
- **Advanced Rare Earth – Silicon based 2700°F+ capable bond coat developments**
- Development approaches
- Oxidation resistance
- Furnace and thermomecahnical durability

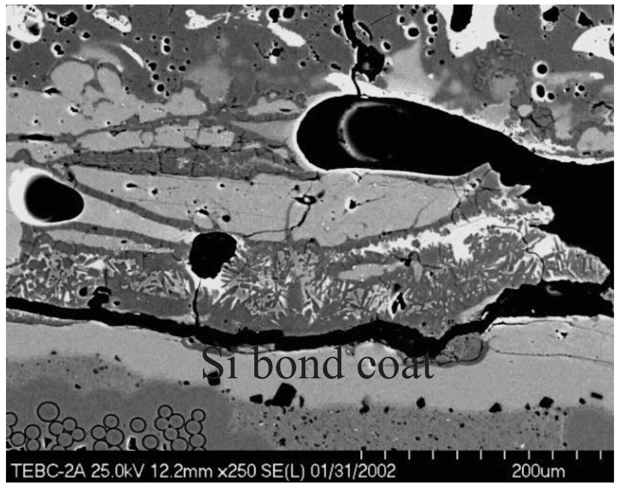
- **Summary**

Use Temperature of Environmental Barrier Coatings Limited by Interface Reactions

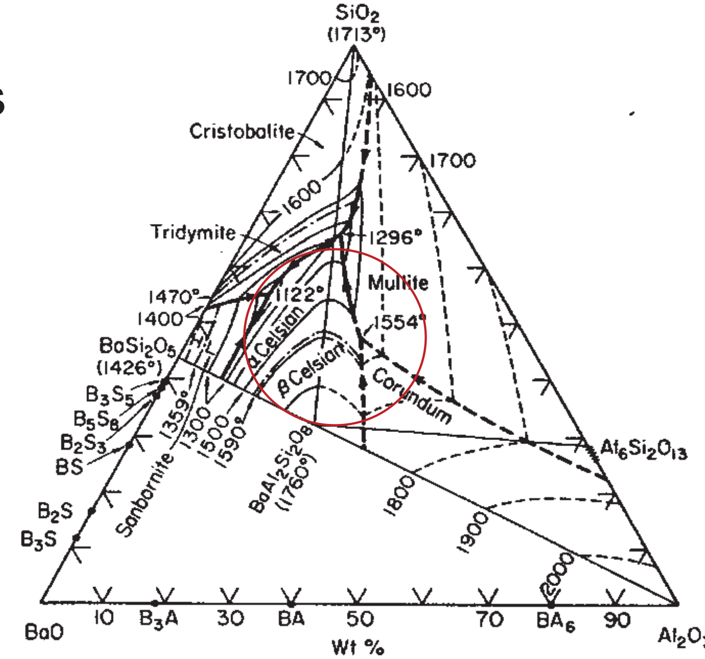
— Significant interfacial pores and eutectic phases formation due to the water vapor attack and Si diffusion at 1300°C

— Heat flux condition further limit the use tempertatures





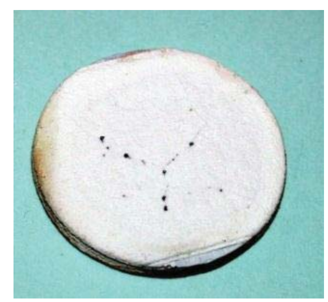
SEM images Interface reactions at 1300°C; total 200 hot hours



BaO-Al_2O_3-SiO_2 ternary phase diagram

Si bond coat after 1350°C, 50 hr furnace test in air; 1” dia plasma sprayed EBC button specimen

Hot pressed BSAS+Si button specimen after 1350°C, 50 hr furnace test in air



Interface Si bond coat melting of selected coating systems, under laser heat flux tests, 1” dia button specimen

NASA EBC and CMC System Development

- Current EBCs limited in their temperature capability, water vapor stability and long-term durability, especially for advanced high pressure, high bypass turbine engines

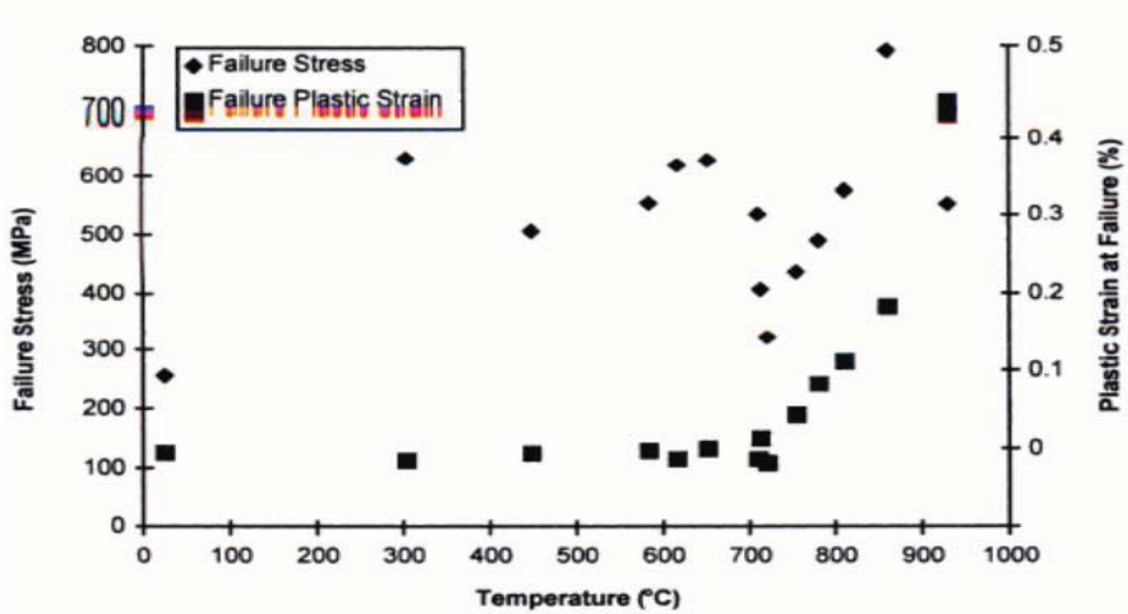
- Advanced EBCs also require high strength and toughness
  - Resistance to heat-flux, high pressure combustion environment, creep-fatigue loading interactions
  - Bond coat cyclic oxidation resistance

- EBCs need improved erosion, impact and calcium-magnesium-alumino-silicate (CMAS) resistance and interface stability
  - Critical to reduce the EBC system Si/SiO_2 reactivity and their concentration tolerance

- EBC-CMC systems need advanced and affordable processing
  - Using existing infrastructure and alternative coating production processing systems, including Plasma Spray, EB-PVD and Directed Vapor EB-PVD, and/or emerging Plasma Spray - Physical Vapor Deposition
  - Affordable and safe, suitable for various engine components

Degradation Mechanisms for Si Bond Coat

- Silicon bond coat melts at 1410°C (melting point)
- Fast oxidation rates (forming SiO_2) and high volatility at high temperature
- Low toughness at room temperature (0.8-0.9 MPa $m^{1/2}$; Brittle to Ductile Transition Temperature about 750°C)
- Low strength and high creep rates at high temperatures, leading to coating delamination
- Interface reactions leading to low melting phases
  - A more significant issue when sand deposit Calcium- Magnesium –Alumino-Siliacte (CMAS) is present
- Si and SiO_2 volatility at high temperature (with and without moisture)



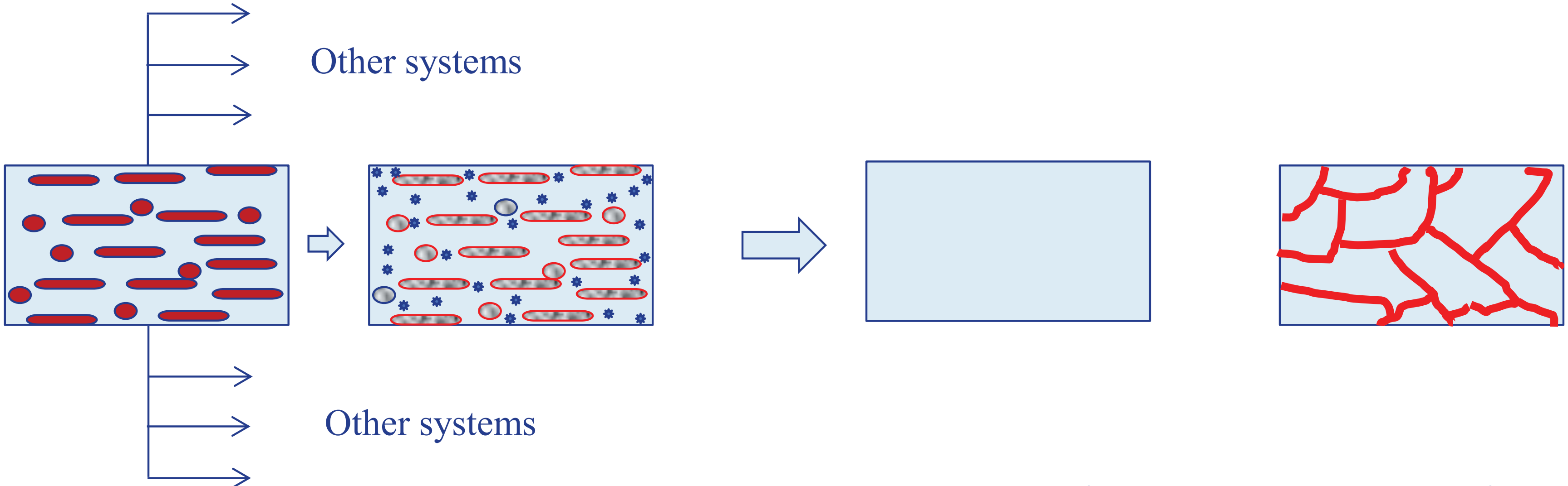
Brittle to Ductile transition in polycrystalline Si

Design Requirements for 2700°F Bond Coat Systems

- High melting point and thermal stability
- Develop slow growing, adherent protective scales
  - High strength and low thermal expansion coefficient scales, and minimum element depletion in the bond coat due to the scale formation essential
- Provide oxidation and environment protection for SiC/SiC CMC substrate
  - Oxidation resistance in all operating temperature range, up to 1600°C, no pesting
- High creep strength and excellent fatigue resistance
  - High resistance to impact, erosion, and CMAS, and environment induced degradations
- Excellent bond strengths (important to provide strong bond for the EBC to the substrate!)
- Thermal expansion coefficient matching to the CMC substrate
- Thermal chemical and thermal mechanical compatibility with EBC and CMC
- Improved bond coat – CMC interface architecture and integration
- Ensure low oxygen activity at the bond coat – CMC interfaces
  - Preferably kinetics controlled and dynamic bond coat systems for durability

Advanced High Temperature and 2700°F+ Bond Coat Development

– Development approach:
- Advanced compositions ensuring high strength, high stability, high toughness
- Bond coat systems for prime reliant EBCs; capable of self-healing



High strength, high stability reinforced composites: HfO_2-Si and a series of Oxide-Si systems

HfO_2-Si based and minor alloyed systems for improved strength and stability

Advanced 2700°F bond coat systems: RE-Si based systems

Advanced 2700°F bond coat systems: RE-Si based Systems, grain boundary engineering designs and/or composite systems -

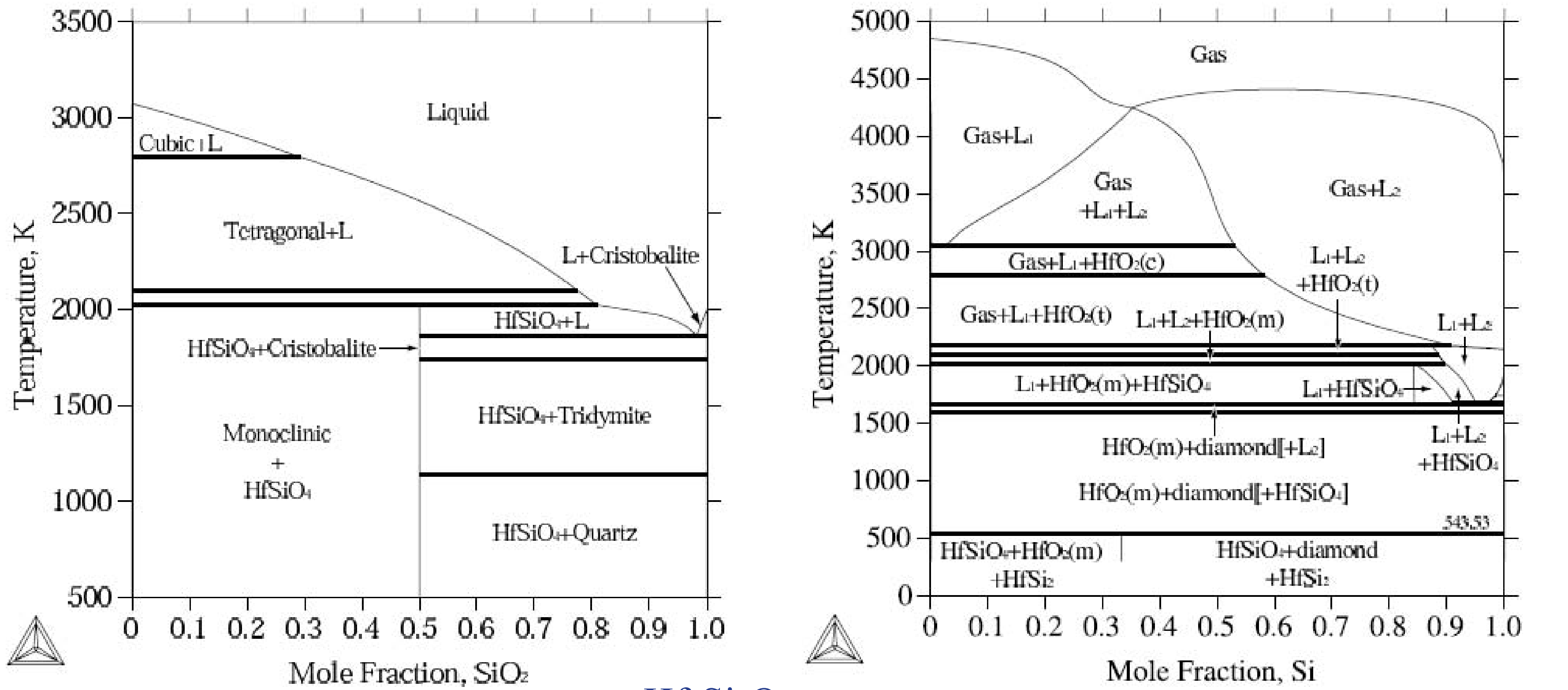
HfO_2-Si systems

Advanced 2700°F+ Bond Coat systems

HfO_2-Si Bond Coats for Improved Temperature Capability, and High Temperature Strength

- A relatively low cost bond coat system, and APS and EB-PVD processing capable
- Excellent oxidation resistance, also ensuring low oxygen activities at the EBC-CMC interface
- Upper use temperature 1400°C and can be up to 1482°C
- SiO_2-$HfSiO_4$-HfO_2 phase system at very high temperature
- Thermal expansion coefficient ~ 5.5 $\times 10^{-6}$ /K
- Rare earth metal or other dopants added for improved stability

Dongwon Shin et al. / Computer Coupling of Phase Diagrams and Thermochemistry 0 (2008) 1–0 10



Hf-Si-O system

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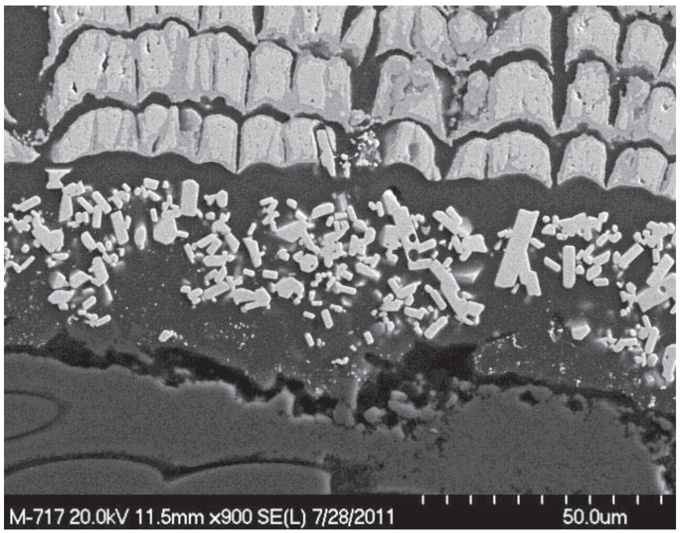
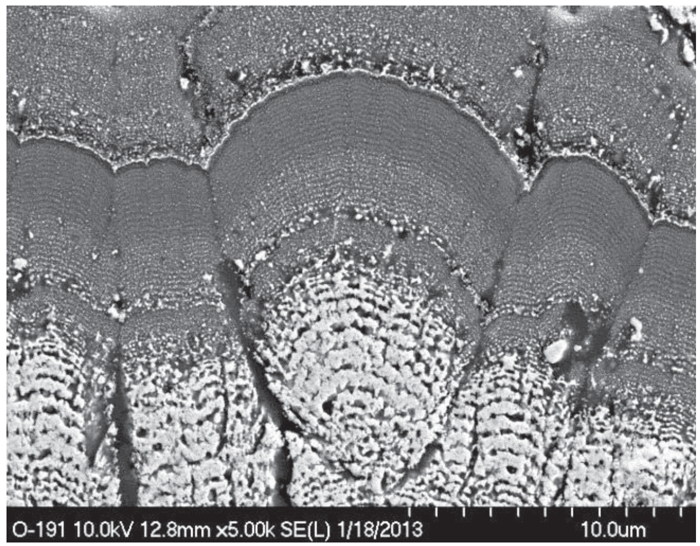
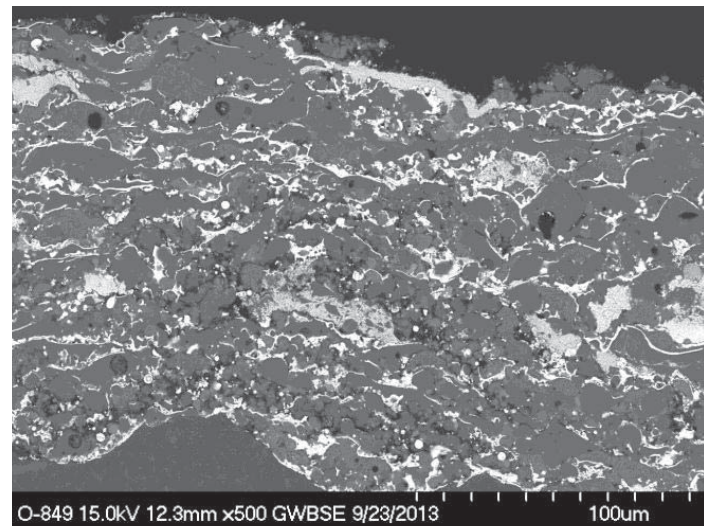




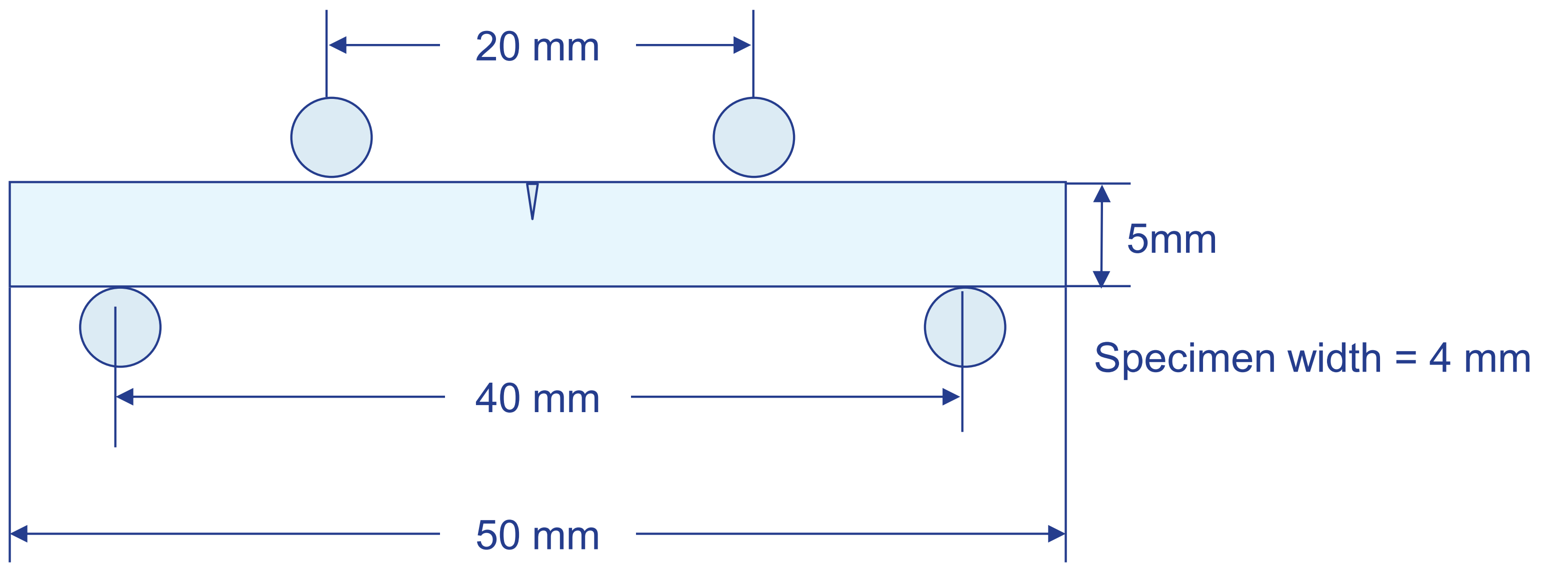


HfO_2-Si and alloyed EBC bond coats using EB-PVD processing: achieving higher temperature capability

Plasma sprayed HfO_2-Si EBC bond coat

Experimental: Mechanical Specimen Configurations

- Flexural specimens with dimensions 4x5x50 mm, machined from hot-pressed air plasma spray (APS) HfO_2-Si powders (billets size 75mmx50mmx10mm); test spans 20 and 40 mm
  - Using ASTM standards 1161 and 1211
  - Si concentration range from 25 to 70wt% in the HfO_2-Si systems
- The non-notched bar specimens used for strength, and creep testing
- Single edge V-notched beam (SEVNB) specimens used for toughness tests
- Test temperature range room temperature, 1200 up to 1500°C



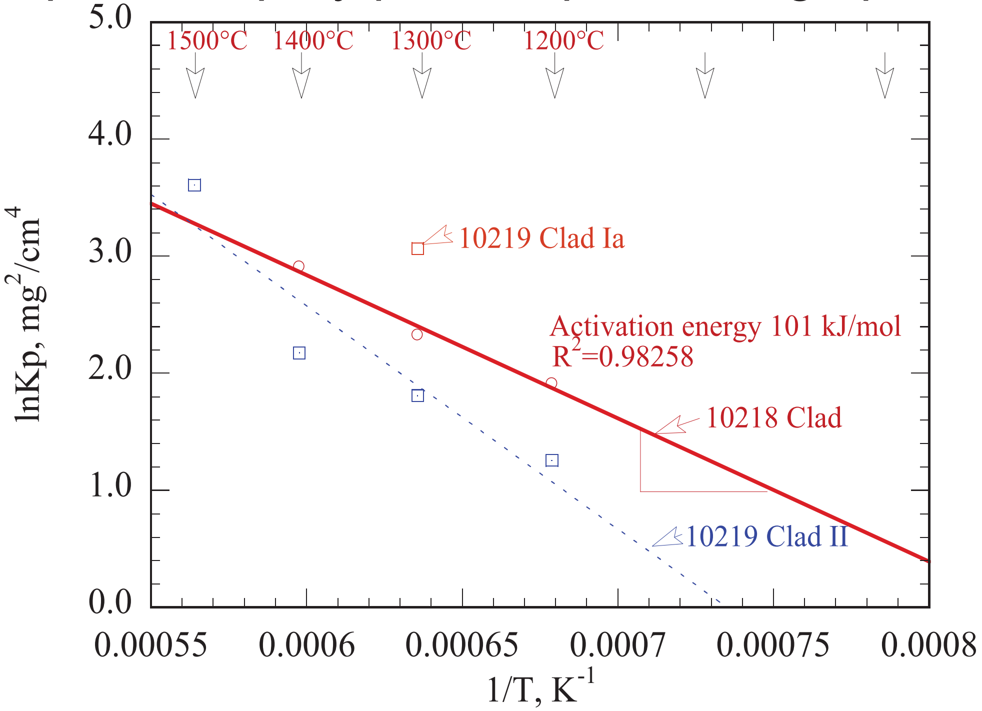
Experimental: Oxidation and Durability Tests

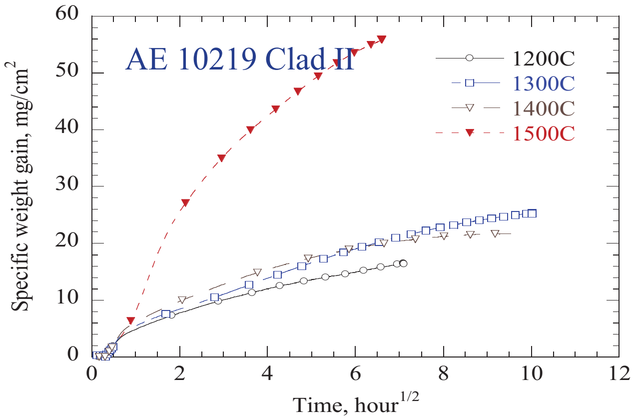
- Test specimens with dimensions 25 mm diameter disc specimens for oxidation, laser heat flux and furnace cyclic test (FCT)
- Test specimens with dimensions 152x12.7 mm dog-bone, and 76x12.7mm for tensile creep rupture and fatigue tests

- Tests were conducted including
  - Thermogravimetric analysis (TGA)
  - FCT test
  - Laser + steam/CMAS water vapor cyclic test
  - Thermomechanical creep and fatigue

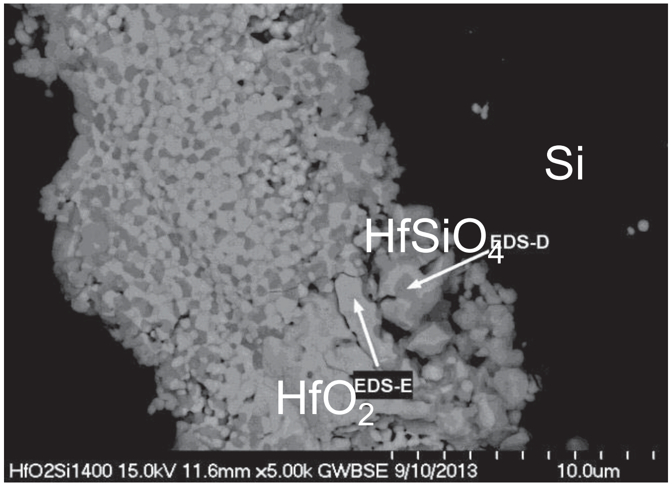
Oxidation Resistance of HfO_2-Si

- TGA weight change measurements in flowing O_2
- Parabolic oxidation kinetics generally observed
- Solid-state reaction is also involved with the systems, and more complex behavior at 1400 and 1500°C
- Excellent oxidation resistance and improved oxidation resistance through APS plasma spray powder processing optimization





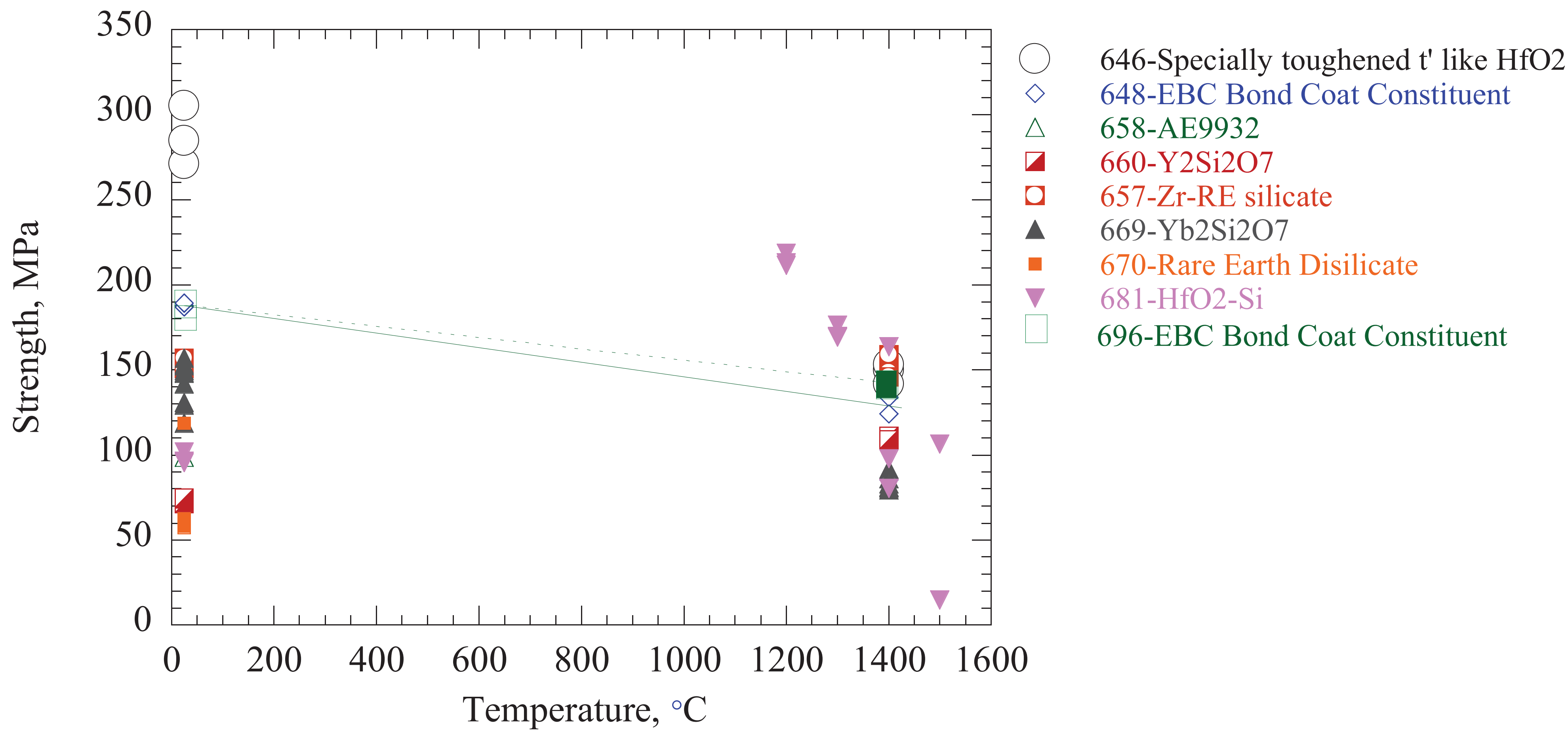
- TGA weight change measurements at various temperatures
- AE 10219 is first Generation HfO_2-30wt%Si composite APS powders used in NASA ERA liner component demonstrations
- AE 10218 is HfO_2-30wt%Si composite APS powders used in NASA ERA liner component demonstrations.
- AE 10219 Clad II is second Generation HfO_2-30wt%Si composite APS powders



Polished specimen microstructure after 1400°C test

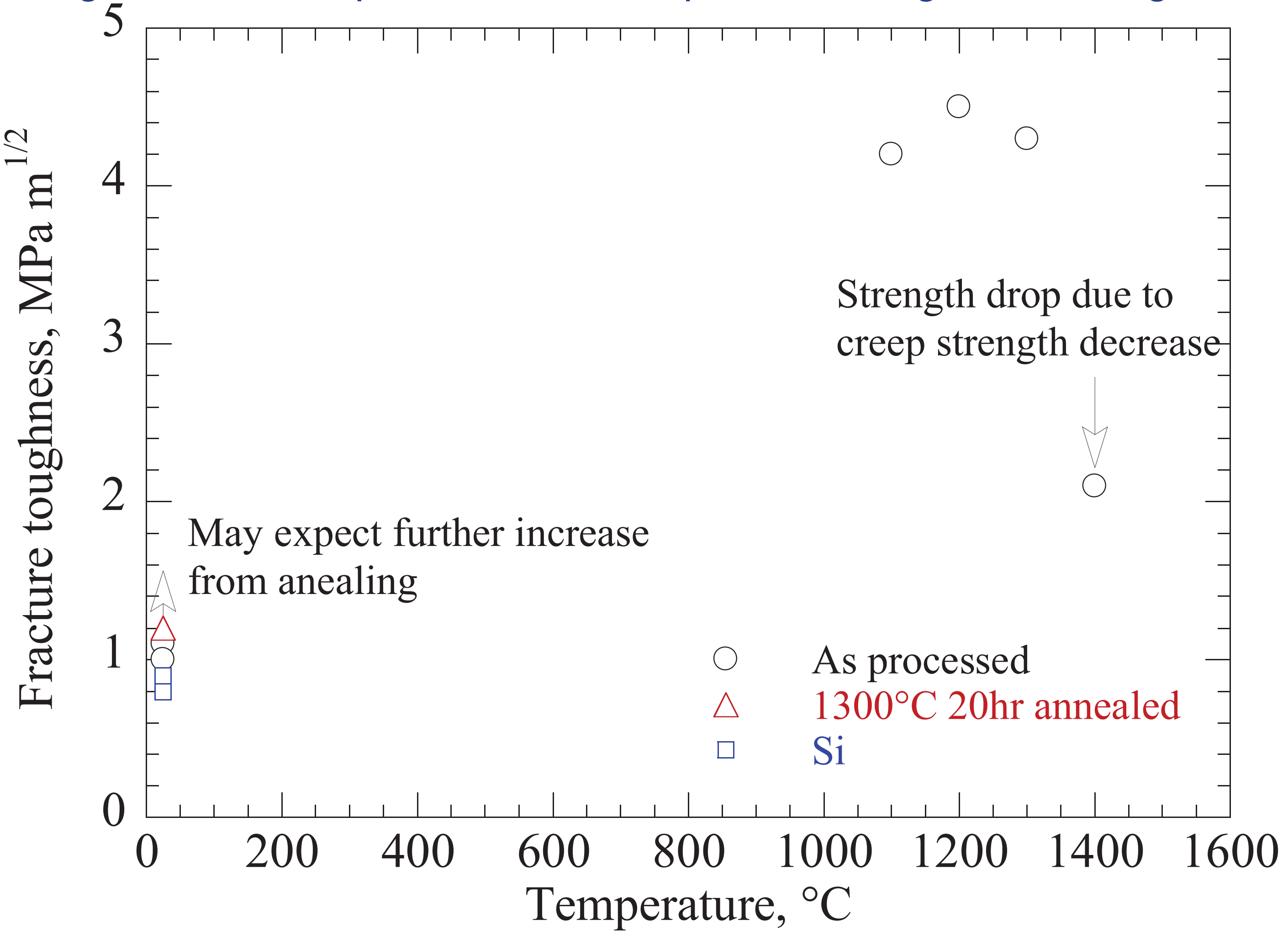
High Strength EBC and Bond Coat Composition Development

– Bond coats and bond coat constituents designed with high strength to achieve the ultimate coating durability, compared with EBCs' strengths
– HfO_2-Si based systems showed high strength and high toughness



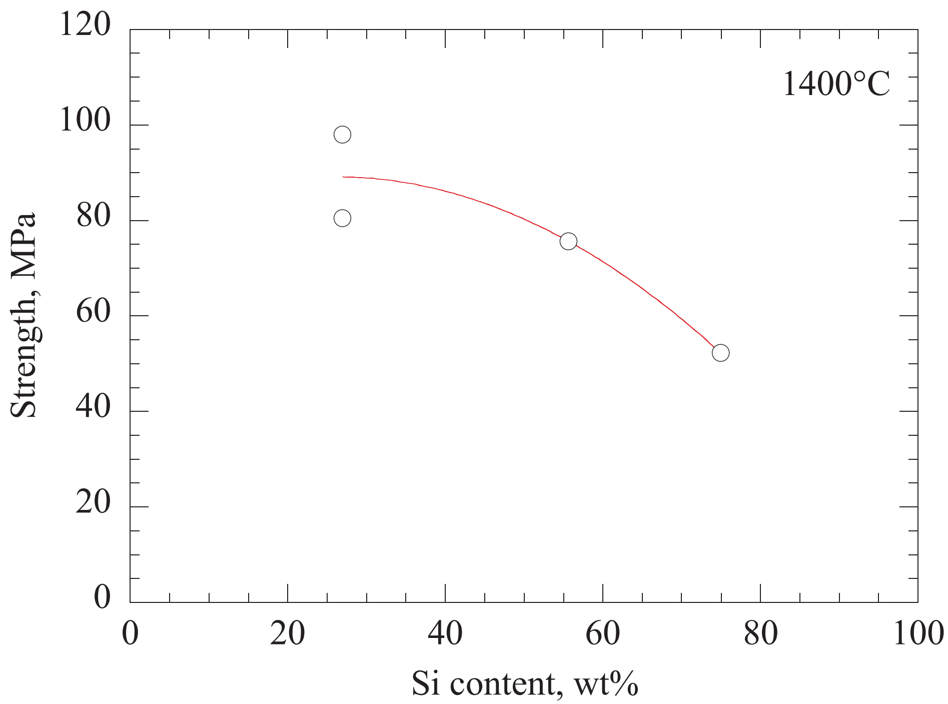
High Toughness HfO_2-Si Bond Coat Composition Development

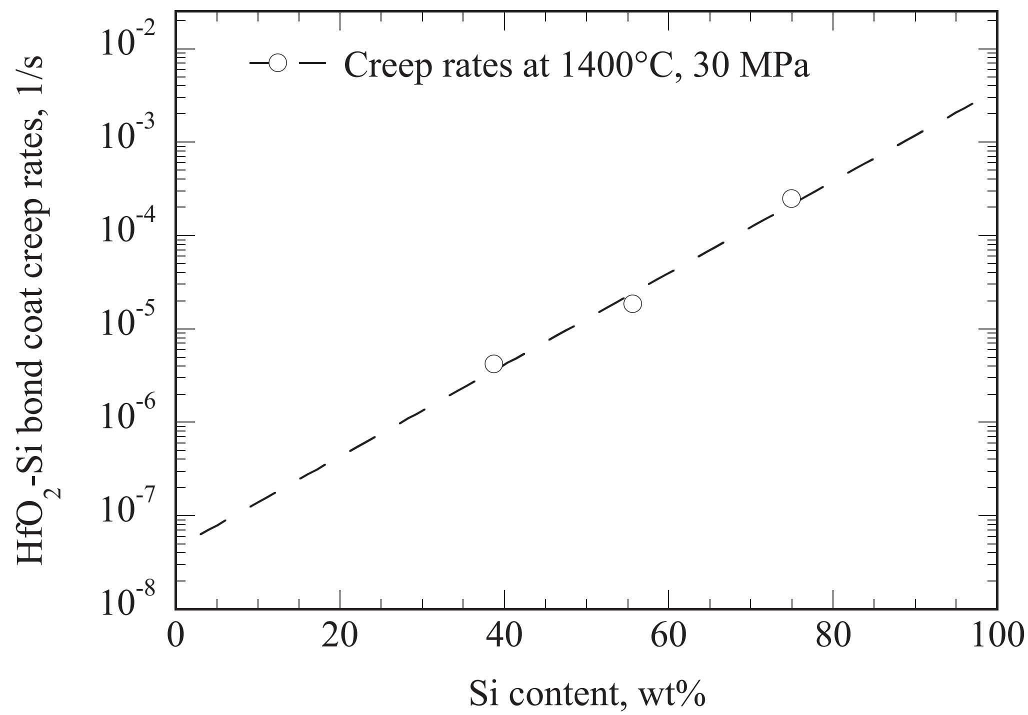
– HfO_2-Si Bond coats showed high toughness
  - Toughness >4-5 MPa $m^{1/2}$ achieved
  - Emphasis on improving the lower temperature toughness
  - Annealing effects on improved lower temperature toughness being studied



Effects of Compositions on HfO_2-Si Strength and Creep Rates

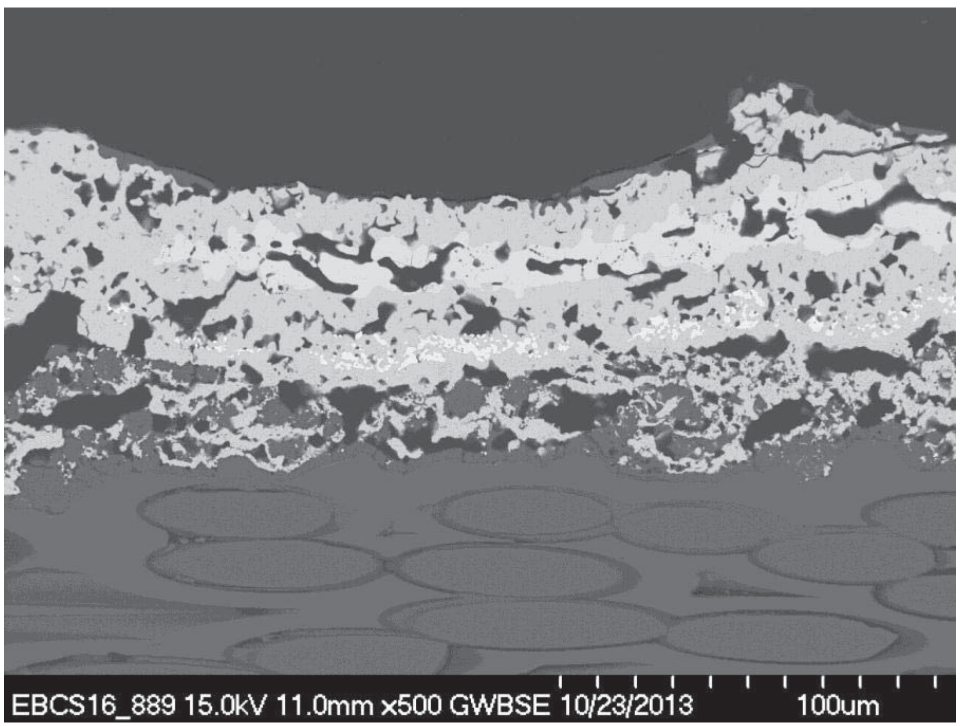
- The composites coatings have improved creep strength, and creep resistance at high temperatures
- *Increased HfO_2-$HfSiO_4$ contents improve high temperature strength and creep resistance*

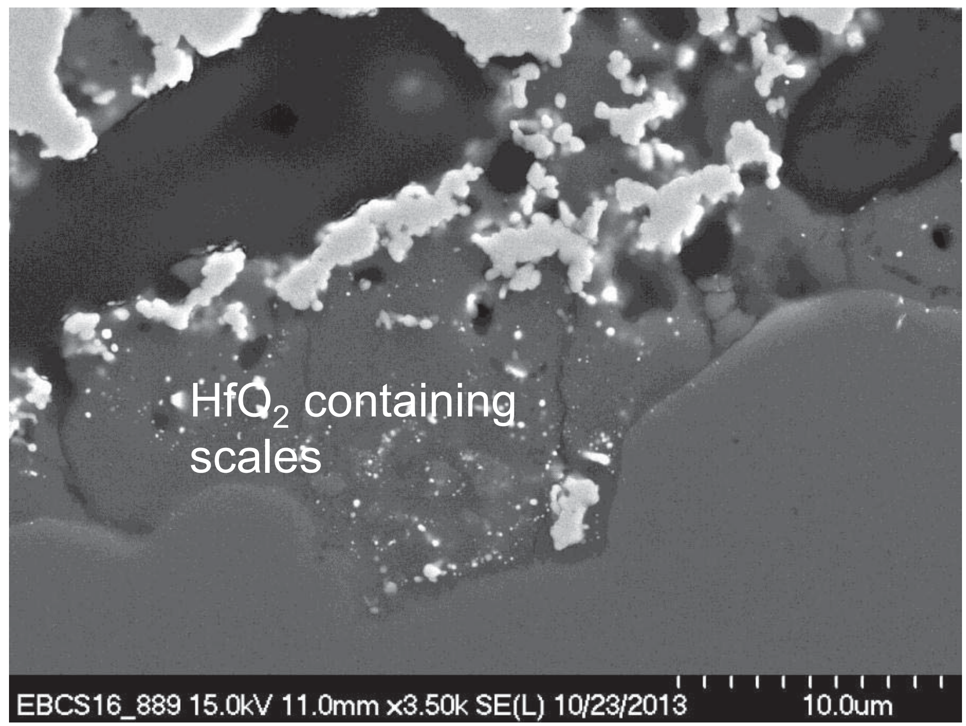




HfO_2-Si/Ytterbium Silicate EBC System Furnace Cyclic Durability Test at 1500°C

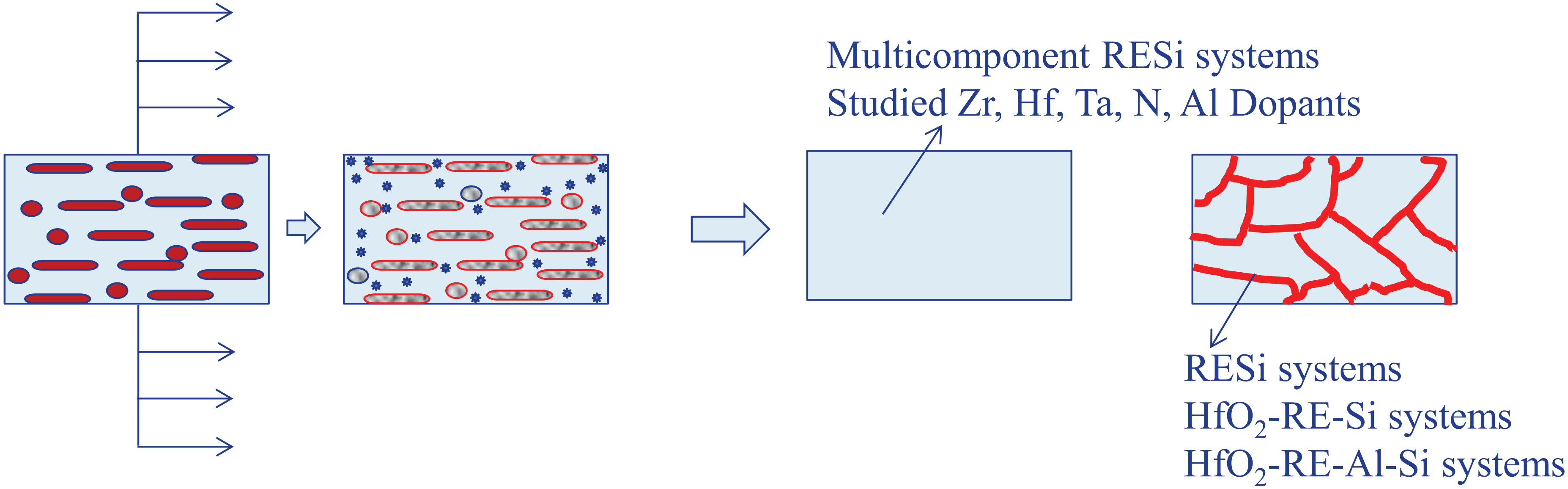
- Coating processed using Triplex Pro plasma spray processing, not necessarily fully optimized
- Long-term furnace cyclic durability tested 1500°C for 500 hr in air
- EBC with HfO_2-Si bond coat adherent (no any spallation) after testing
- Excellent oxidation resistance in protecting SiC/SiC
- SiO_2 loss in ytterbium silicate EBC (some area became ytterbia), and in the HfO_2-Si bond coat
- Some HfO_2 containing scales may be stable





Advanced 2700°F+ Bond Coats (Beyond HfO_2-Si)

– Development approach:
  - Advanced compositions ensuring high strength, high stability, high toughness
  - Bond coat systems for prime reliant EBCs; capable of self-healing



High strength, high stability reinforced composites: HfO_2-Si and a series of Oxide-Si systems

HfO_2-Si based and minor alloyed systems systems

Advanced 2700°F bond coat systems: RE-Si based systems

Advanced 2700°F bond coat systems: RE-Si based Systems, grain boundary engineering designs and/or composite systems -

HfO_2-Si systems

Advanced 2700°F+ Bond Coat systems

2700°F+ Advanced EBC Bond Coat Developments: Rare Earth Silicon Systems and Effect of Dopants

– Ytterbium, Yttrium and Gadolinium – Silicon or Silicide systems

- **Controlled silicon compositions and oxygen activities** to achieve good thermal expansion match with SiC/SiC CMCs and EBCs, and high melting points and stability
- **Focusing on multicomponent high temperature based systems** to ensure high temperature capability, oxidation resistance and durability
- **Emphasizing chemically and mechanically compatibility** with SiC/SiC CMCs and various environmental barrier coatings, *no free-standing silicon phases in composition designs*
- **Low temperature oxidation resistance and pesting issues** are also addressed in the developments

NASA Advanced 2700°F Silicide Based Bond Coats – System Processing for Various Component Applications

- Advanced systems developed with high Technology Readiness Levels (TRL)
- Composition ranges studied mostly from 50 – 80 atomic% silicon
  - PVD-CVD processing, for composition downselects - also helping potentially develop a low cost CVD or laser CVD approach
  - Compositions initially downselected for selected EB-PVD and APS coating composition processing
  - Viable EB-PVD and APS systems downselected and tested; development new PVD-CVD approaches

PVD-CVD

YSi	YbGdYSi	GdYSi
ZrSi+Y	YbGdYSi	GdYSi
ZrSi+Y	YbGdYSi	GdYSi
ZrSi+Ta	YbGdYSi	GdYSi
ZrSi+Ta	YbGdSi	GdYSi-X
HfSi + Si	YbGdSi	GdYSi-X
HfSi + YSi	YbGdSi	
HfSi+Ysi+Si	YbGdSi	
YbSi	YbGdSi	
	YbSi	
HfSi + YbSi		
GdYbSi(Hf)		
YYbGdSi(Hf)	YbYSi	
	YbHfSi	
	YbHfSi	
	YbHfSi	
	YbHfSi	
	YbHfSi	
	YbSi	

EB-PVD

HfO_2-Si; REHfSi

APS

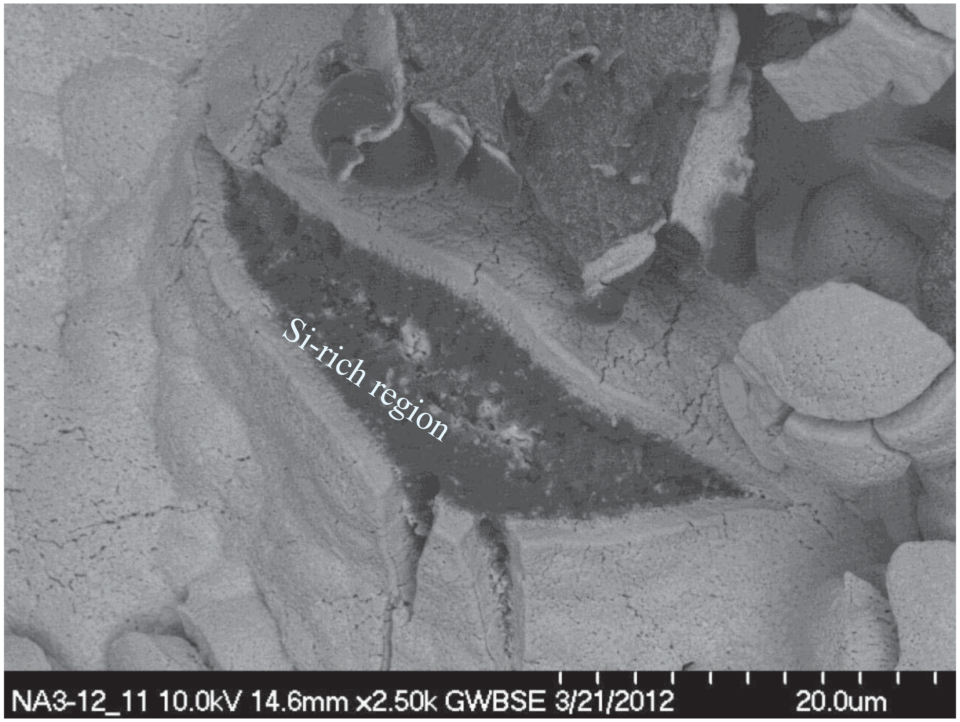
YSi+RESilicate	
YSi+Hf-RESilicate	
9869 Hf-RESilicate	Used in ERA components as part of bond coa system
10157 Hf-RE-Al-Silicate	Used also in ERA components Used in ERA components as part of bond coa system

Laser/CVD/PVD

REHfSi

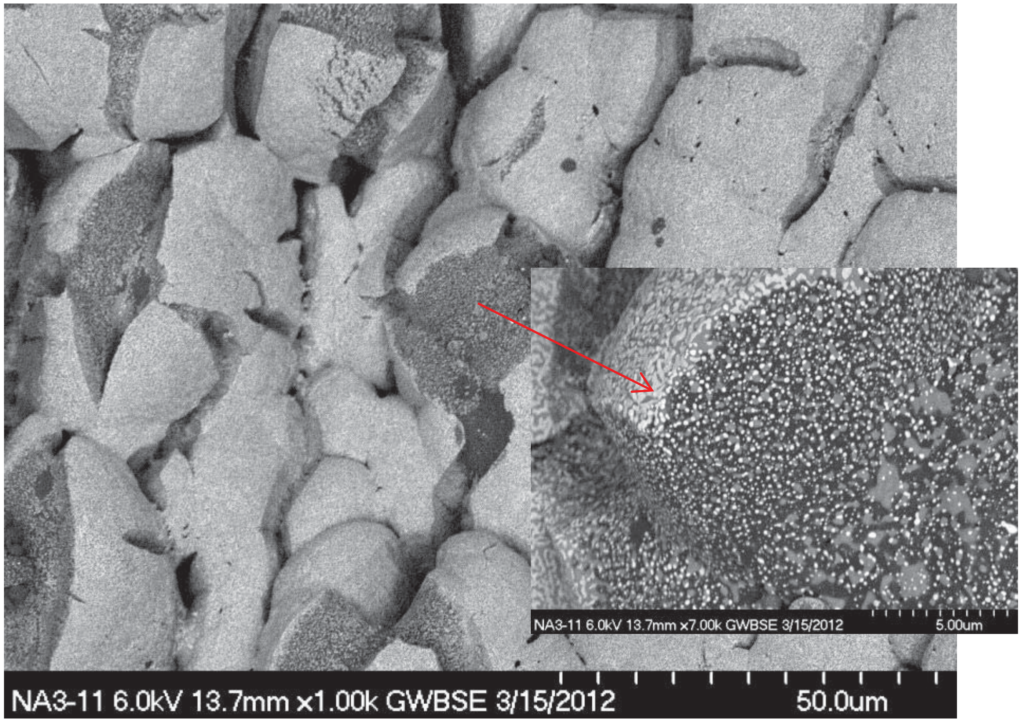
Rare Earth Silicon Systems and Multi-Dopants for Stability

- Silicon-rich phase separations can limit high temperature stability
- Further thermal stability and mechanical strength can be improved by:
  - Composition controls (e.g. optimize silicon contents and addition of dopants)
  - Multi-dopant composition designs for reduced Si/SiO_2 activity



$YbSi_x$ (no additional dopant)
Exposed to 1100°C for 20 h

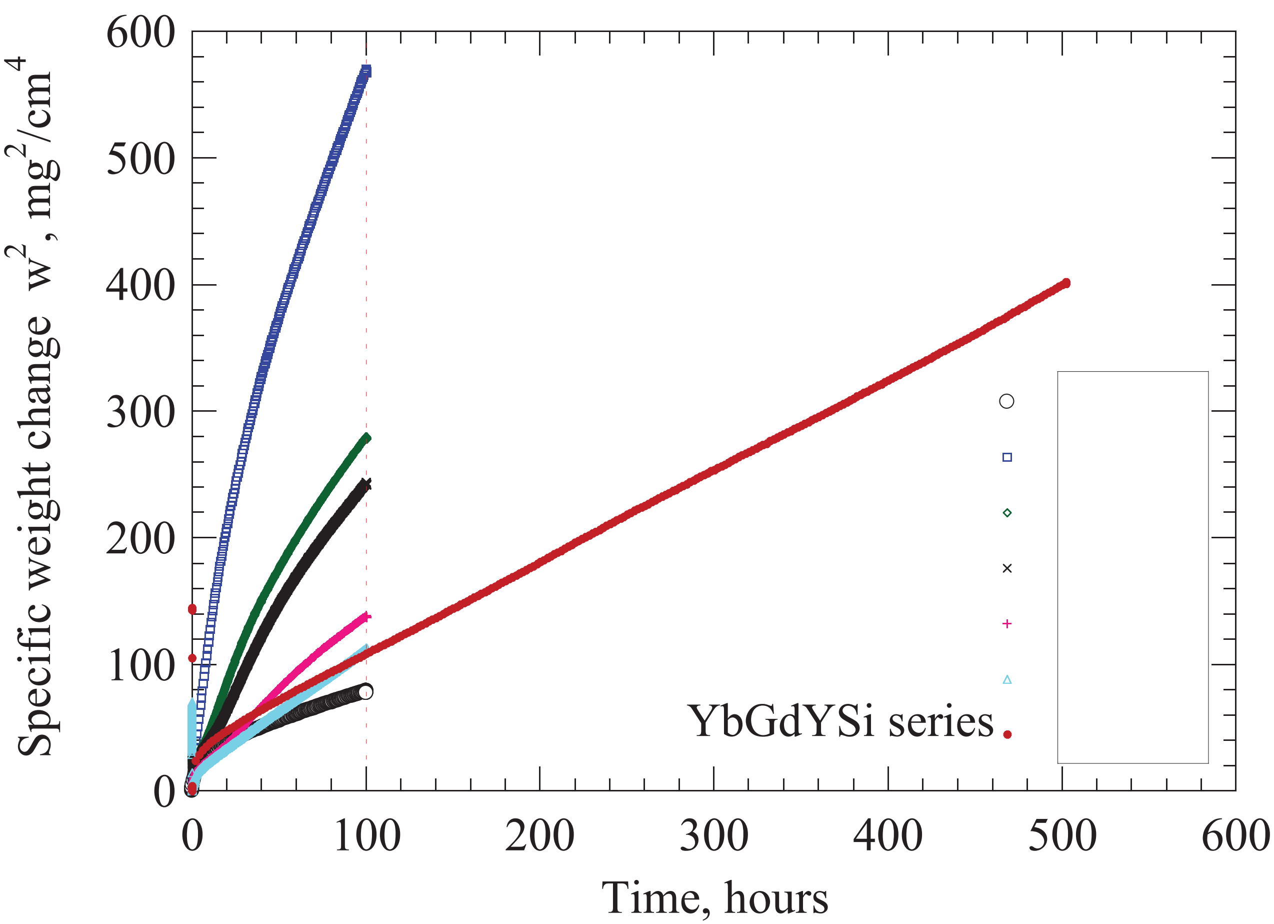
Undoped material: shows separation of Si-rich/silica-rich phase

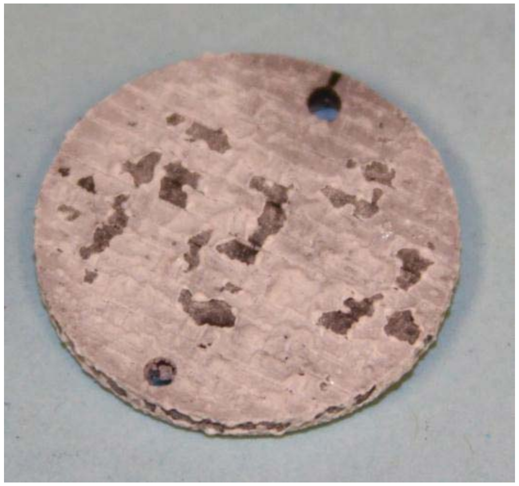


$(Y,Hf)Si_x$
1100°C for 20 h
When dopant included: The Si-rich/silica-rich phases converted to more stable HfO_2 - Hafnium silicate, and yttrium silicate containing phases

Oxidation Kinetics of RE-Si Based EBC Systems

– Thermogravimetric analysis (TGA) performed at 1500°C in flowing dry oxygen
– Bond coat fully coated SiC/SiC (CVI) specimens



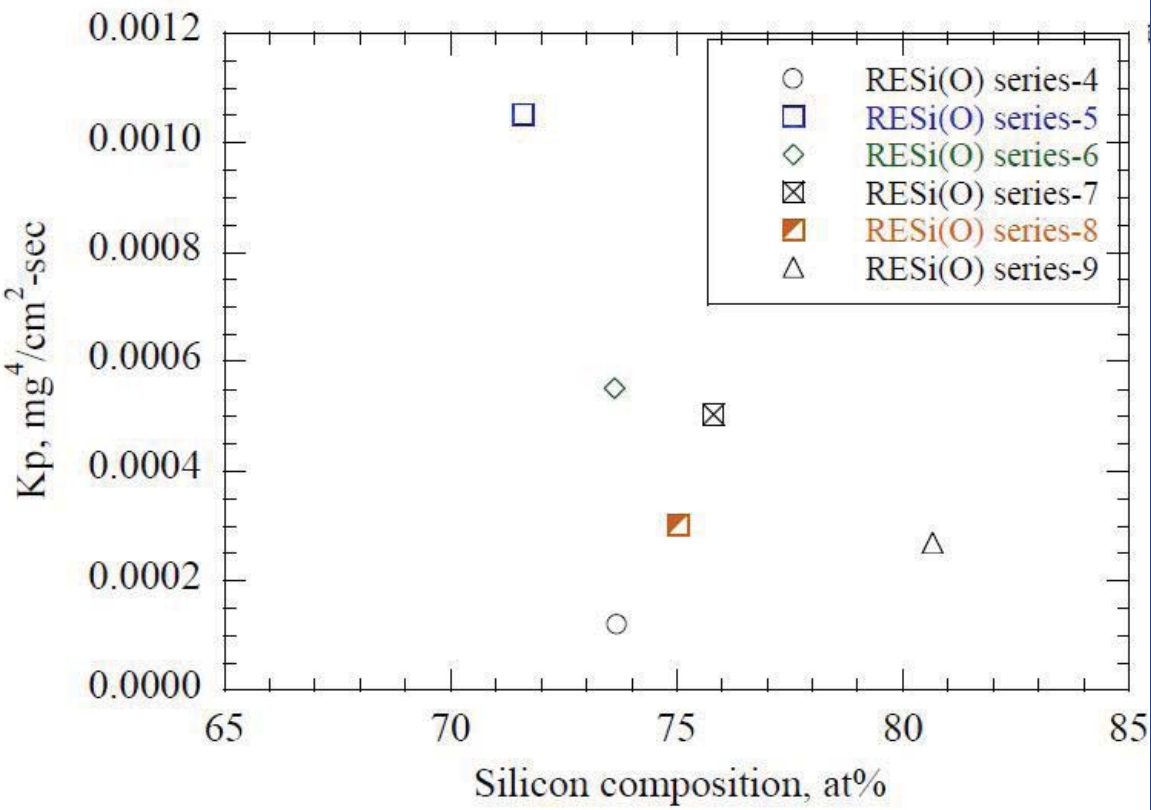


After 500 hr test of an EBC; some surface coating small area spallation after cooling down

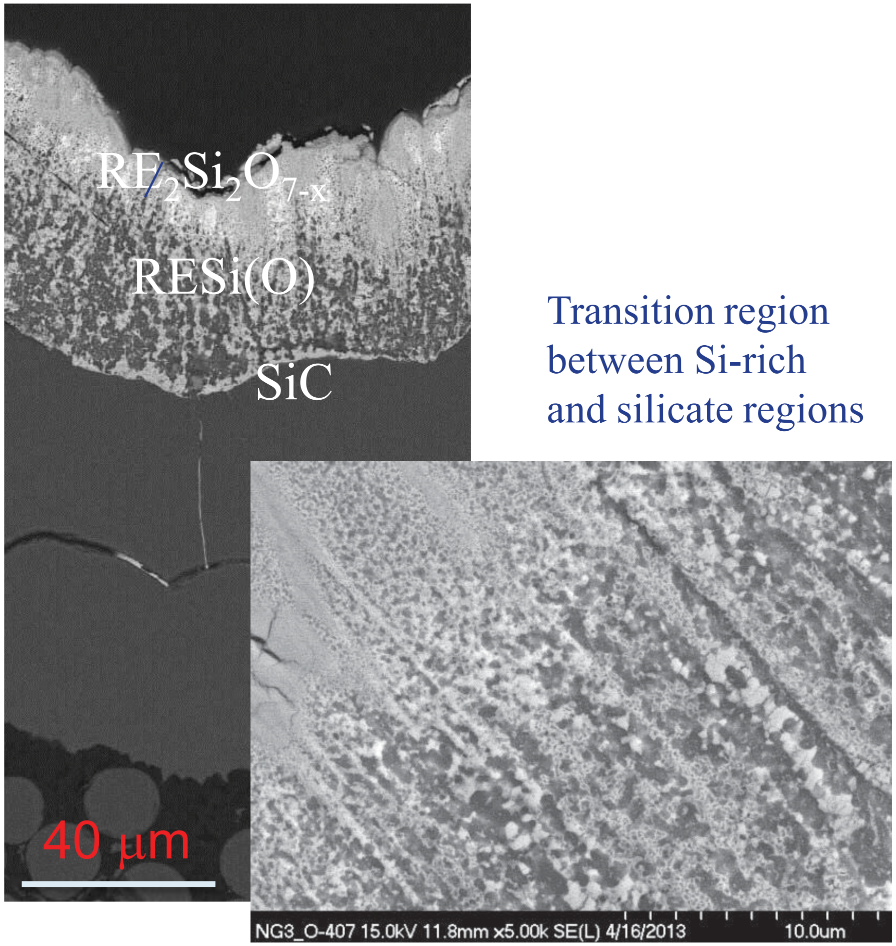
- Lower Si content, Yb-Gd-Y system

Oxidation Resistance of Doped Rare Earth Silicide - Effect of Stoichiometry (oxidation vs. atomic percent Si)

- Thermogravimetric analysis (TGA) in dry O_2 at 1500°C
- "Protective" scale of rare earth di-silicate formed (10-15 micrometers)



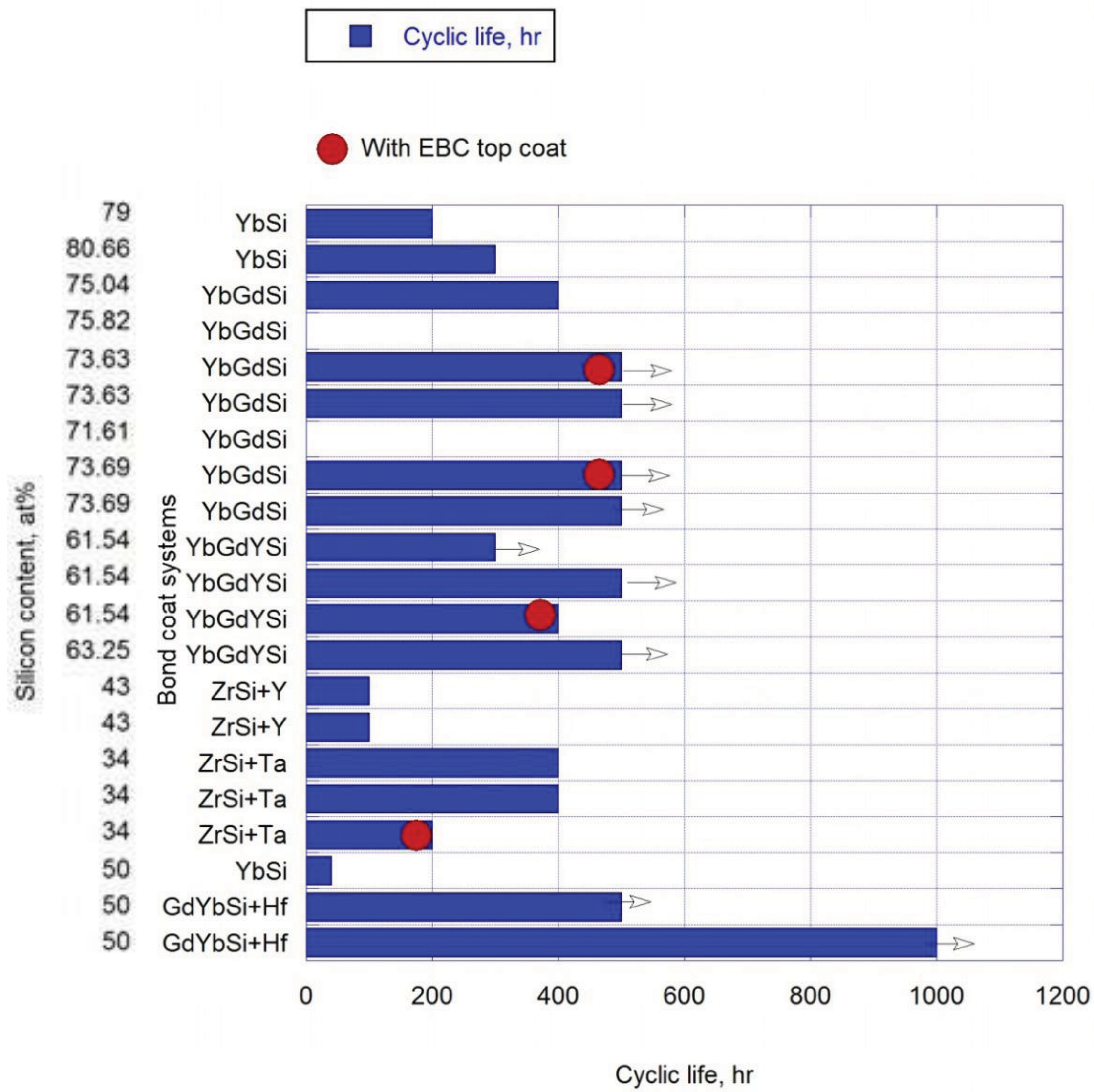
Multicomponent doped RE Silicide system after 100 hr exposure at 1500°C in O_2



Transition region between Si-rich and silicate regions

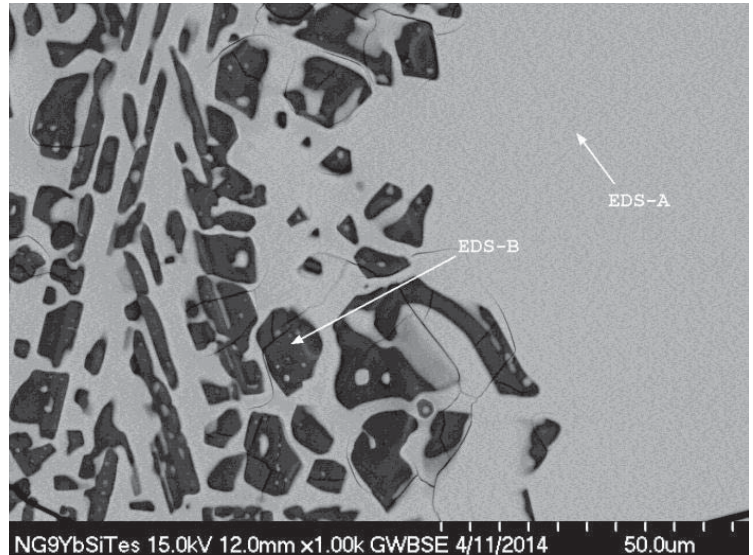
Furnace Cycle Test Results of Selected RESi and ZrSi + Dopant Bond Coats
- Testing in Air at 1500°C, 1 hr cycles

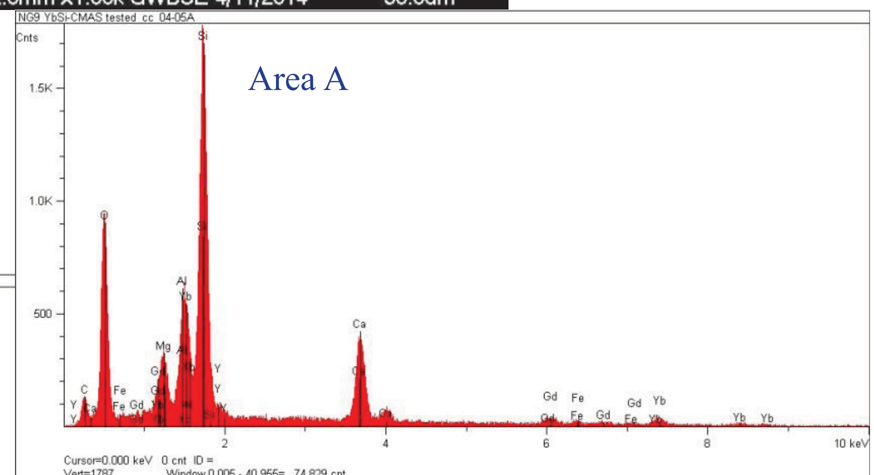
– Multi-component systems showed excellent furnace cyclic durability at 1500°C

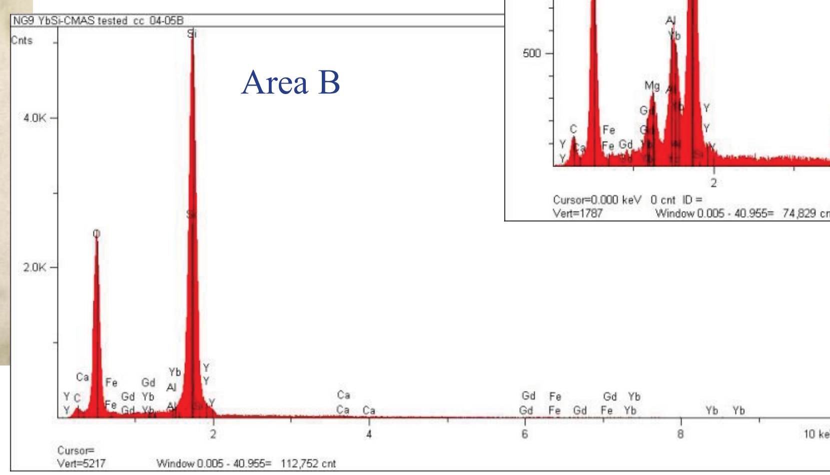


High Stability and CMAS Resistance Observed from the Rare Earth Silicon High Melting Point Coating Compositions

– Demonstrated CMAS resistance of RESi at 1500°C, 100 hr

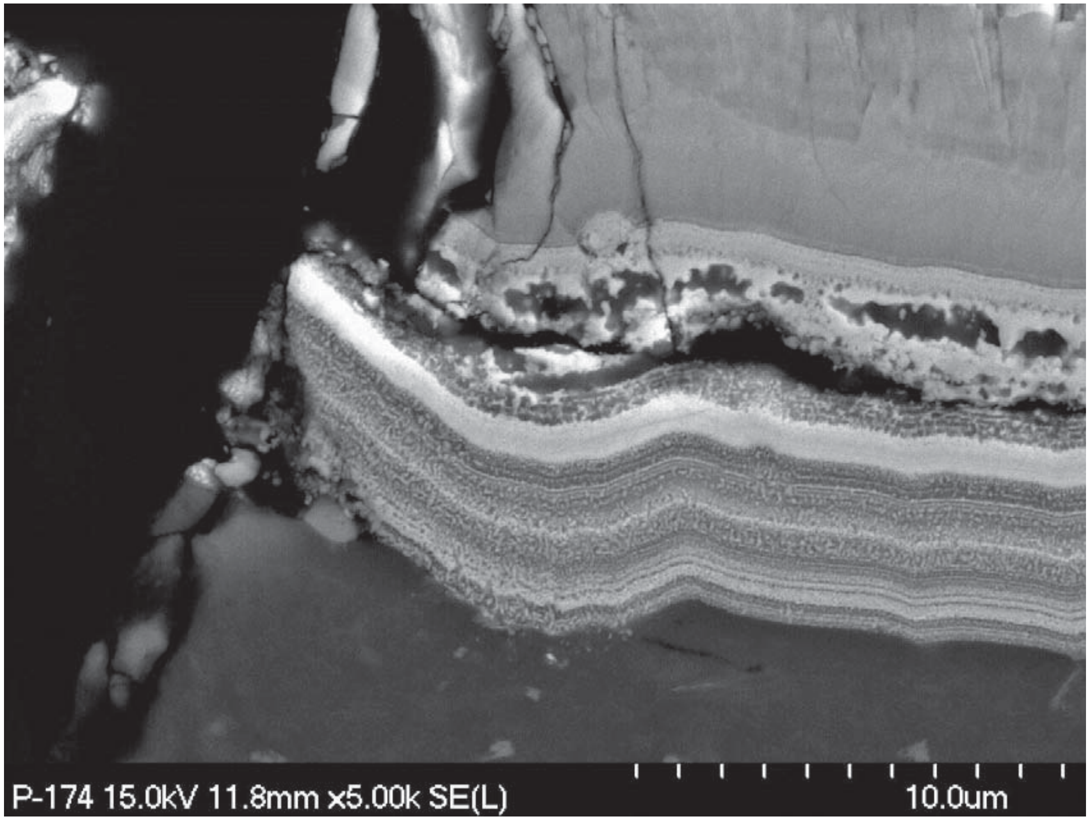






Processing Advancements and Improvements for RE Si Bond Coats in EBC Systems

- Selected EBC system processed by EB-PVD and plasma Spray: Doped RE Si (+Hf) Bond Coat + advanced multi-component EBC Top Coat on woven SiC/SiC CVI-SMI CMC
- Creep testing conducted with 15 ksi load and laser thermal gradient



EBC System after 100 hr creep testing with 2700°F coating surface temperature and 2500°F CMC back temperature

RE(Hf) silicate EBC Top Coat

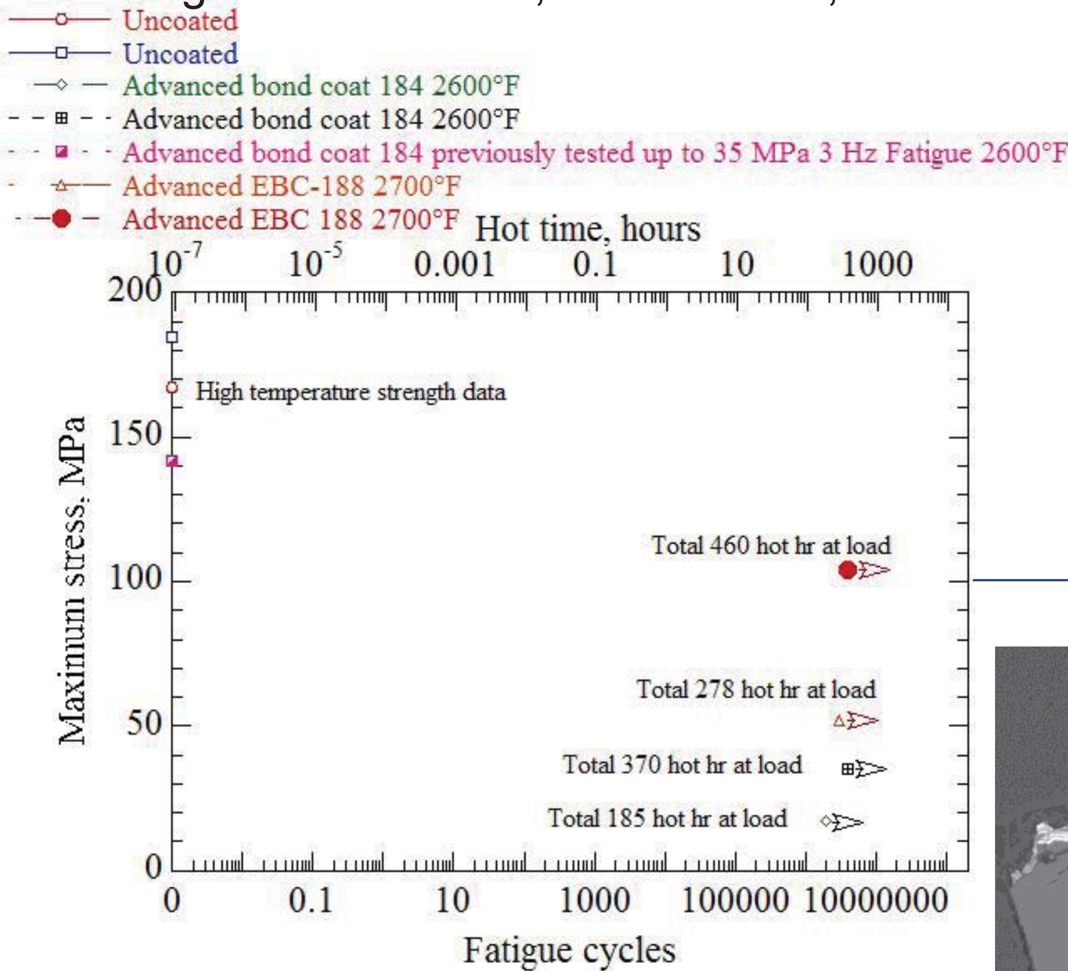
RESi Composite Bond Coat System: Striations indicate EB-PVD layers with compositional variations

Excellent compatibility

Bond coat remains generally well-adhered to CMC substrate after the CMC failure, except some top bond coat composition segregation or processing defective regions

Fatigue Tests of Advanced Bond Coats and EBC Systems

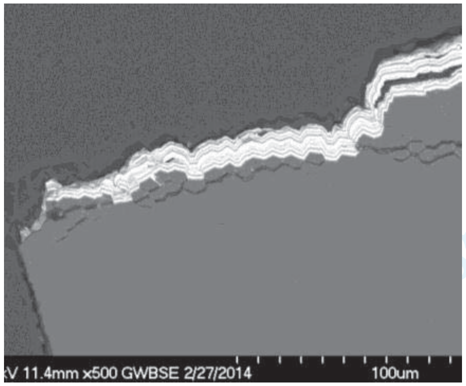
- Uncoated CMCs, Bond coat/CMC and EBC/Bond Coat/CMC systems tested flexural fatigue tests with 15 Ksi loading
- Heating provided by steady-state laser
- Strength and Fatigue cycles tested
- Fatigue tests at 3 Hz, 2600-2700°F, stress ratio 0.05, surface tension-tension cycles

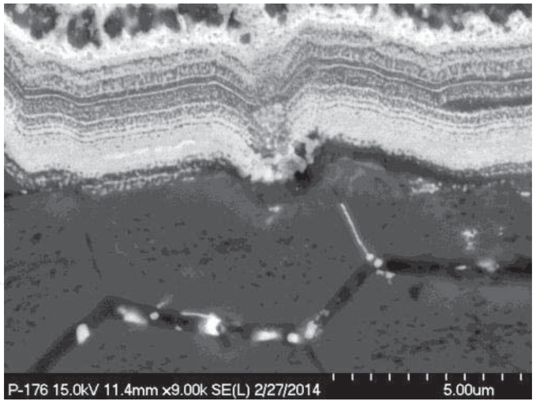


Tested, SA Tyrannohex with bond coat only

Tested, SA Tyrannohex with EBC system 188

Achieved long-term fatigue lives (near 500 hr) with EBC at 2700°F





Tested specimen cross-sections

Summary

- Advanced HfO_2-Si and Rare Earth - Silicon based bond coat compositions developed
- The coatings showed excellent oxidation resistance and protection for CMCs
- HfO_2-Si showed excellent strength, fracture toughness, its upper use temperature may be limited to 1400°C due to higher silica activity, in particular in the CMAS environments
- The initial silicon content range of the Rare Earth-Silicon coatings was down-selected, multicomponent systems designed for further improved stability
- The rare earth – silicon based coatings showed 1500°C operating temperature viability and durability on SiC/SiC ceramic matrix composites
- The rare earth – silicon based coatings compositions will be down-selected; and further processing optimization planned

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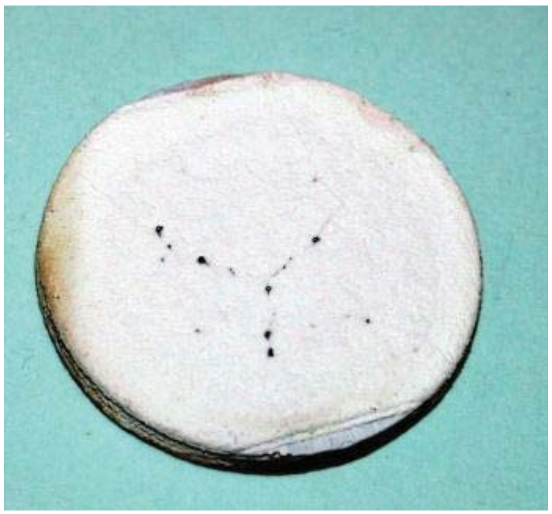
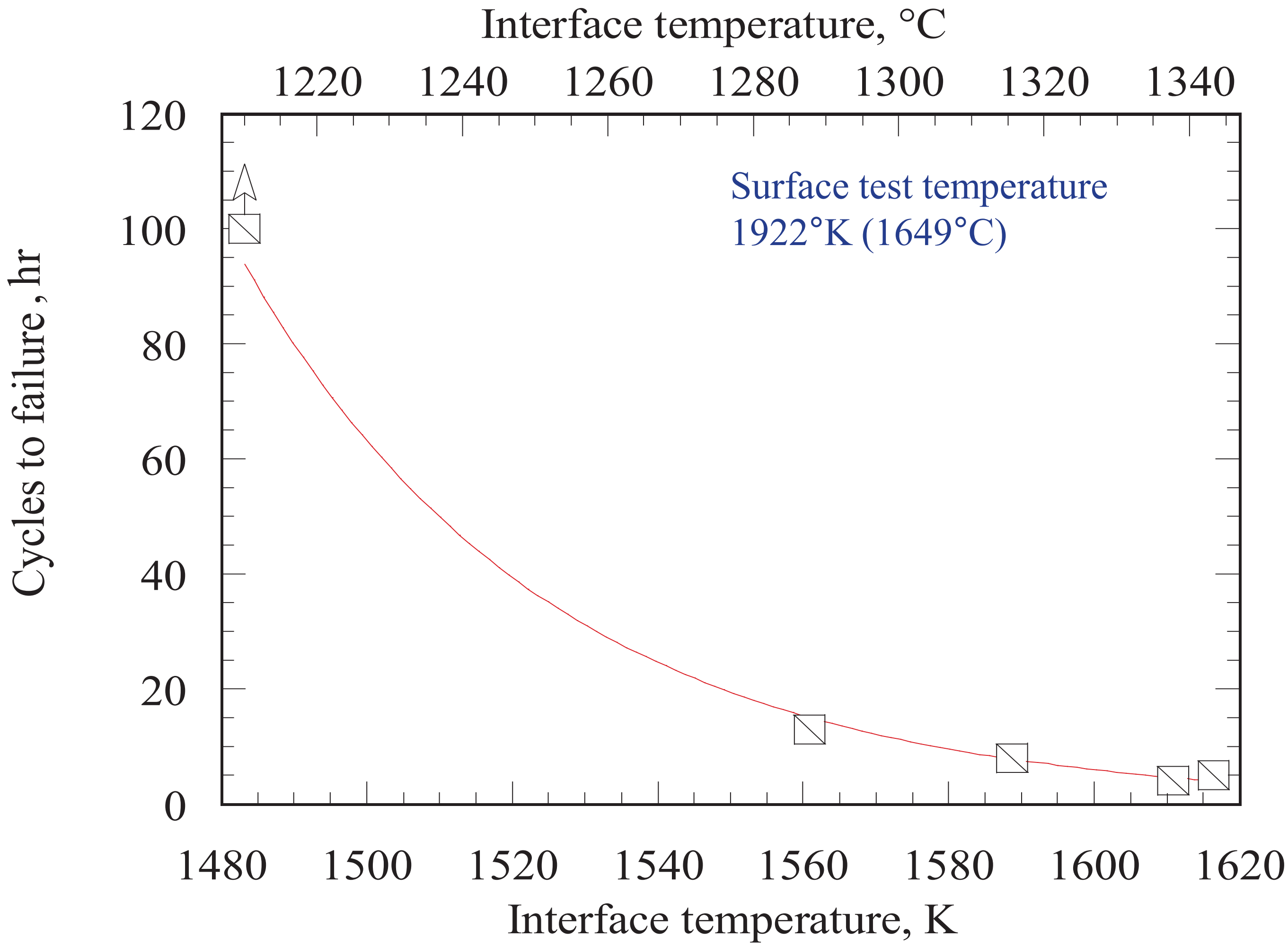
Use Temperature of Environmental Barrier Coatings Limited by Interface Reactions - Continued

- Various advanced EBC/mullite/mullite+BSAS/Si coating systems heat flux tested
- Accelerated spallation under heat flux tests observed
- Significantly reduced cyclic durability due to bond coat melting



Interface Si bond coat melting of selected coating systems, under laser heat flux tests, 1” dia button specimen



Effect of interface temperatures on heat flux cyclic life

X-ray Phase Studies of Hot Pressed HfO_2-Si systems

– X-ray phase showed HfO_2-$HfSiO_4$ some with silica phase near surface

Sample: HfO2-Si 1200°C, 50 hr

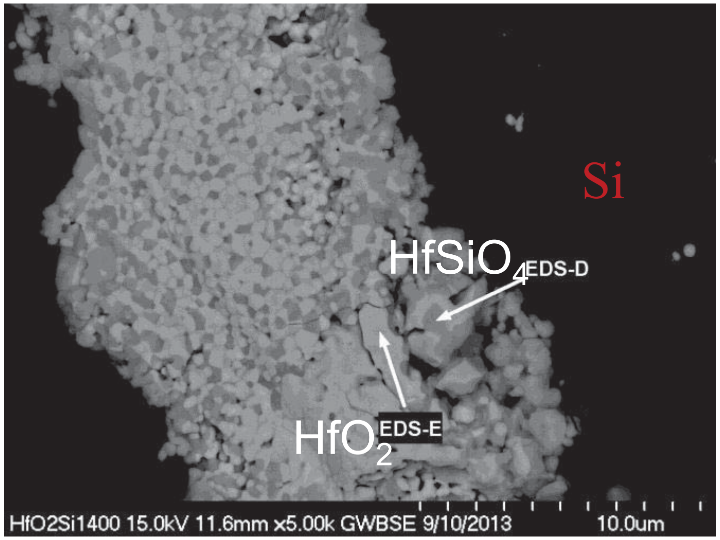
Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Hf O2	Hafnium Oxide	Monoclinic	04-006-7680	27
Hf (Si O4)	Hafnium Silicate	Tetragonal	04-008-6813	7
Si	Silicon	Cubic	04-006-2527	66

Sample: HFO2-Si 1300°C, 100 hr

Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si	Silicon	Cubic	04-006-2527	46
Hf O2	Hafnium Oxide	Monoclinic	04-006-7680	23
Hf (Si O4)	Hafnium Silicate	Tetragonal	04-008-6813	15
Si O2	Silicon Oxide	Tetragonal	04-012-1126	16

Sample: HfO2-Si 1400°C, 50 hr

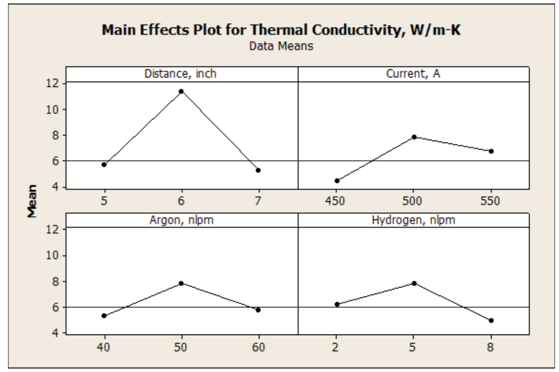
Chemical Formula	Compound Name	Crystal System	Ref. Code	SemiQuant [%]
Si	Silicon	Cubic	04-006-2527	47
Hf O2	Hafnium Oxide	Monoclinic	04-006-7680	20
Hf (Si O4)	Hafnium Silicate	Tetragonal	04-008-6813	11
Si O2	Silicon Oxide	Tetragonal	04-012-1126	22

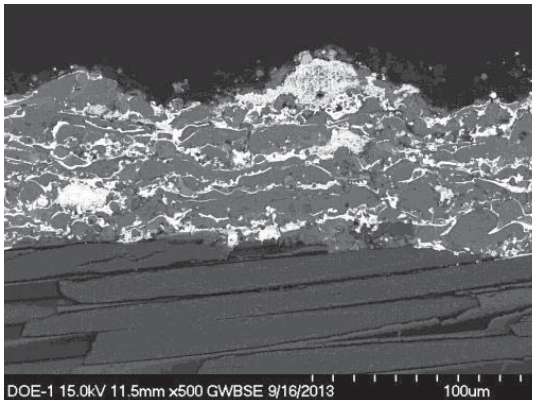


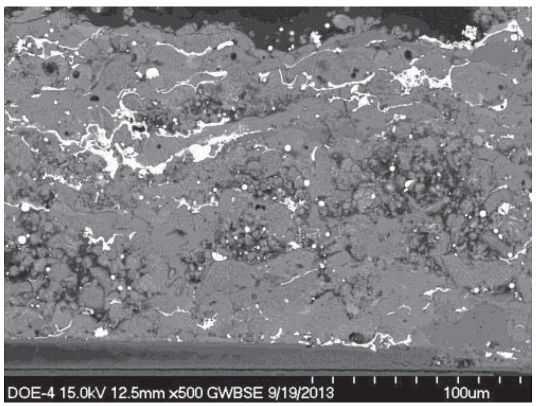
Polished specimen microstructure

Advanced APS HfO_2-Si Processing Optimizations

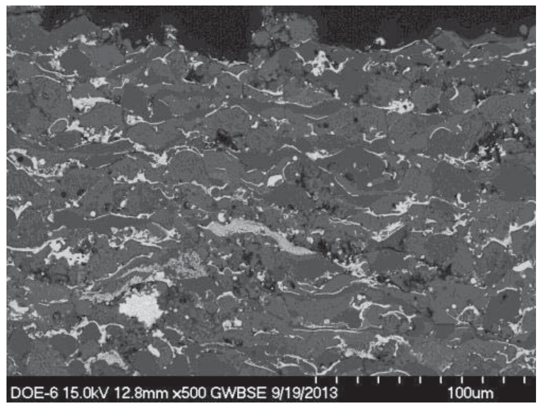
– Design of Experiments (DoE) to help achieve improved density and phase distributions – Processing performed using Triplex Pro, at Sulzer Metco

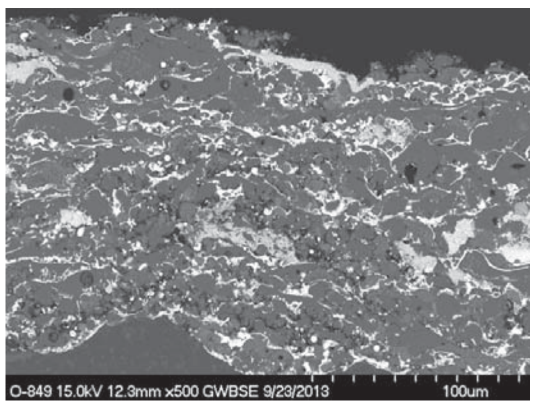


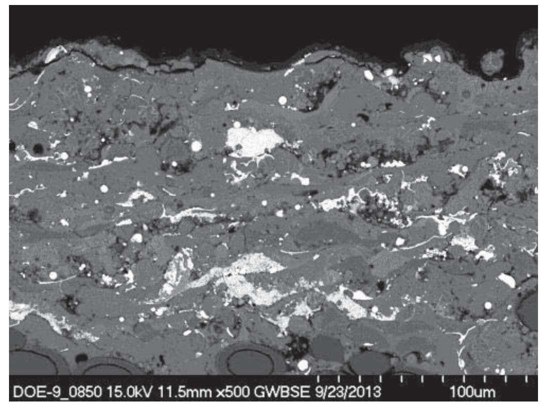


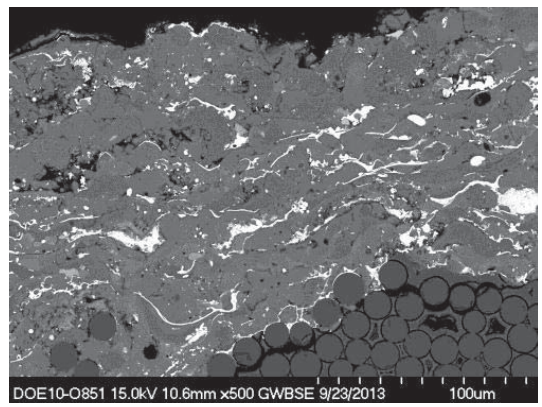


Spray parameters optimized



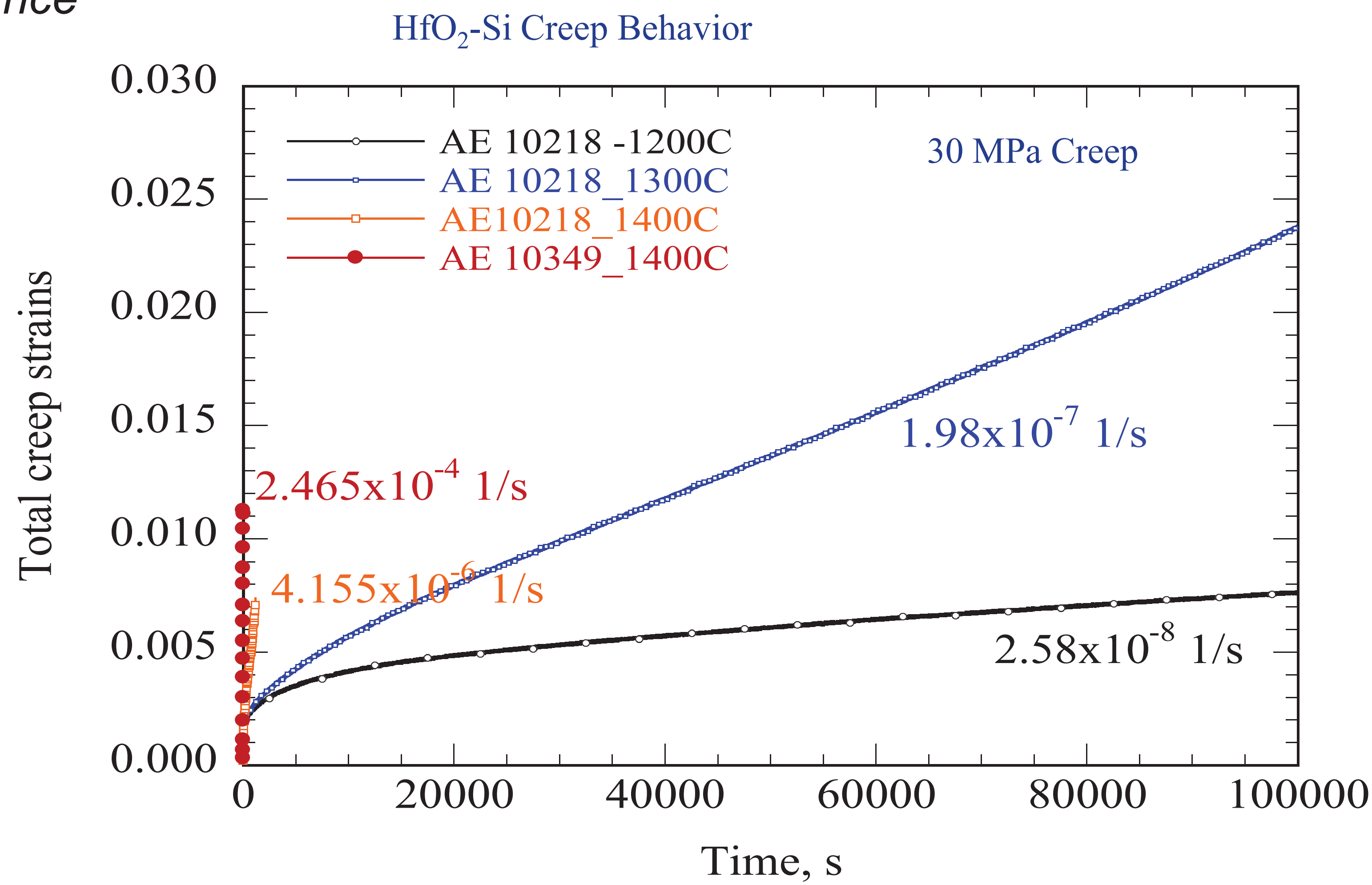






Effects of Compositions on Strength and Creep Rates - Continued

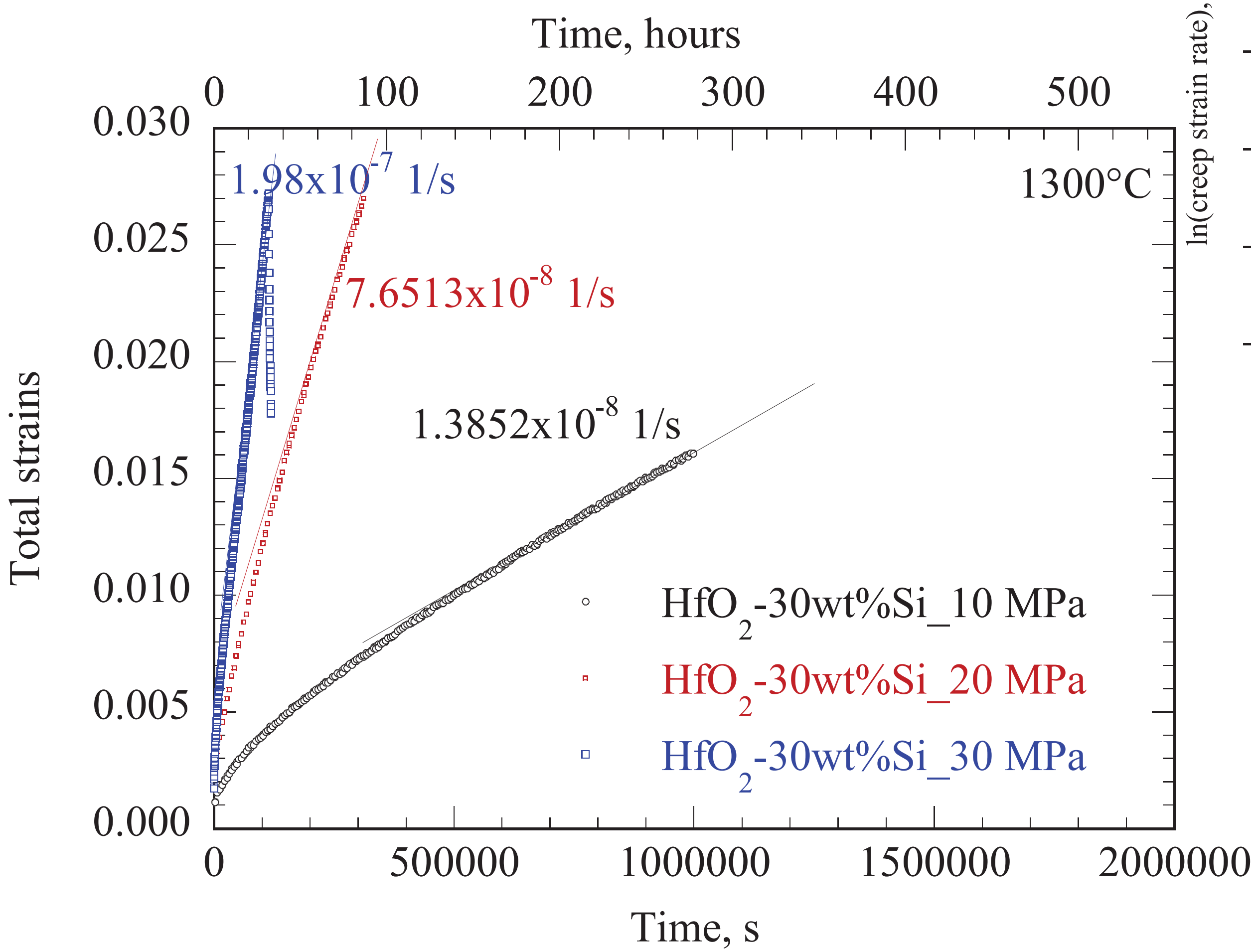
– The composites coatings have high strength, and improved creep resistance at high temperatures
– *Increased HfO_2-$HfSiO_4$ contents improve high temperature strength and creep resistance*

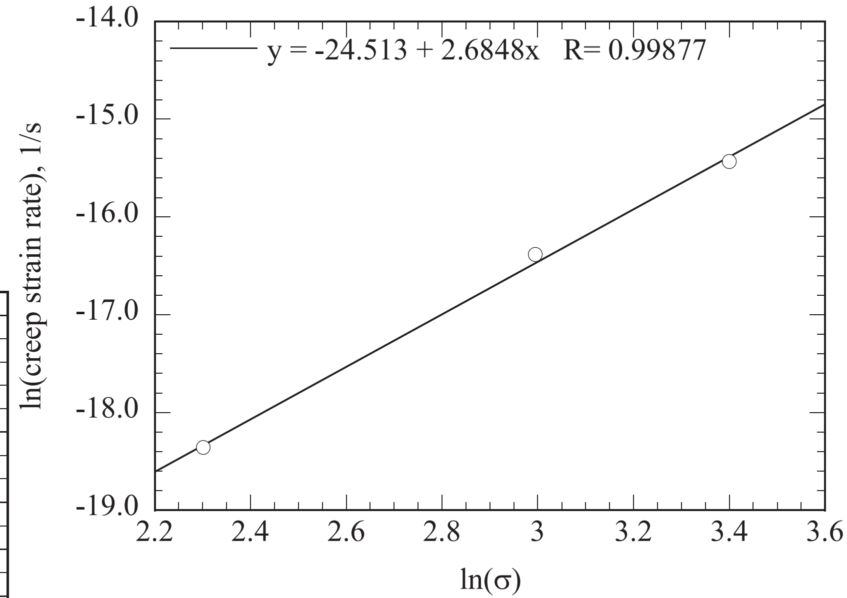


- AE 10218 is HfO_2-30wt%Si composite APS powder pressed specimens.
- AE 10349 is HfO_2-70wt%Si composite APS powders

Creep Behavior of HfO_2-Si Bond Coat – Stress Dependence

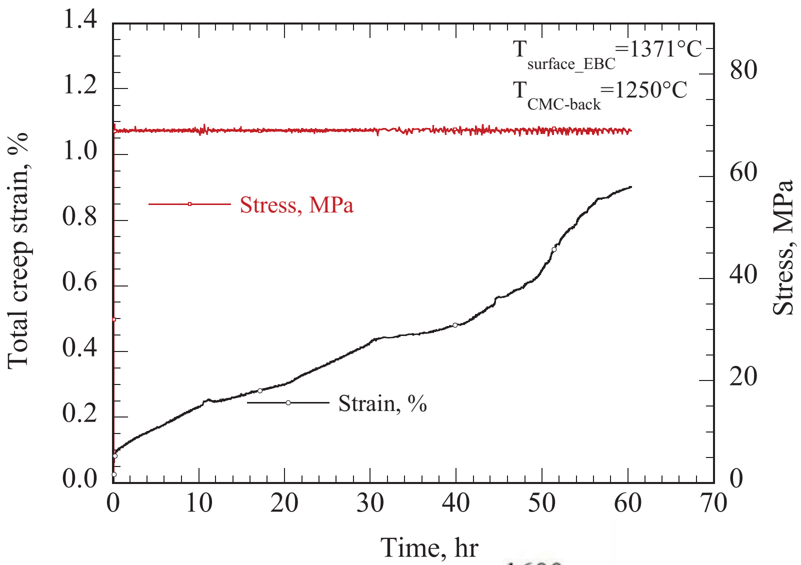
- Creep rate stress dependence studied
- Stress exponents determined to be 2.6

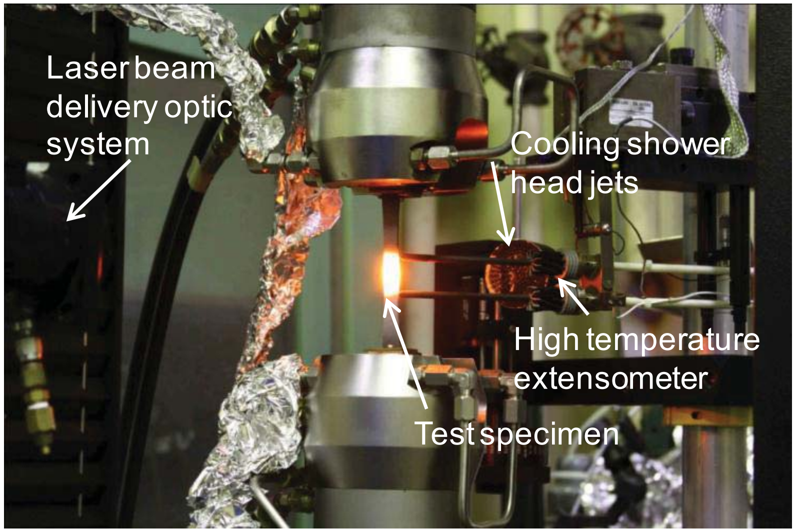


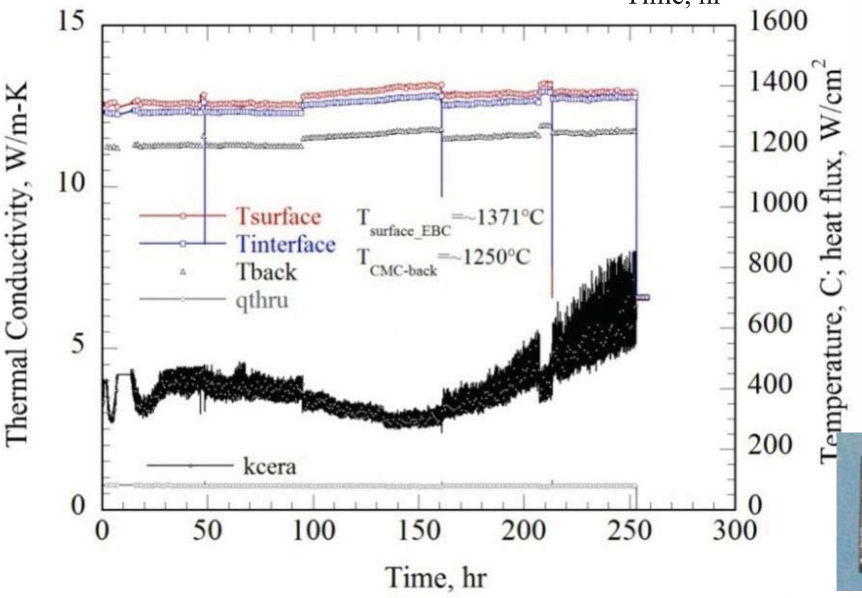


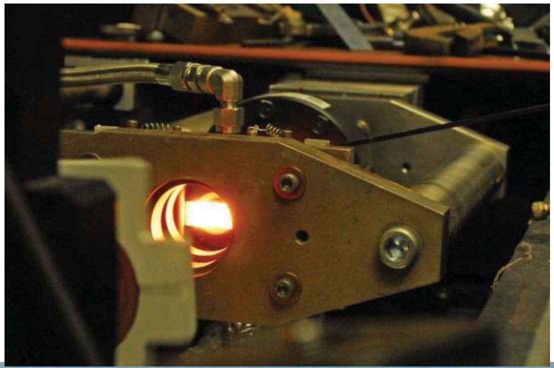
HfO_2-Si EBC Durability Studies at Up to 1500°C

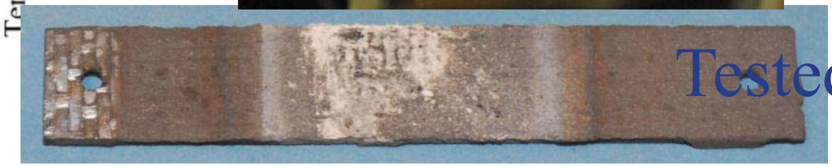
– APS and EB-PVD processing optimizations; long-term durability tested at 1400 – 1500°C











HfO_2-Si Bond Coat 1400°C Thermal Gradient CMAS Tests

– High concentration SiO_2 region may have lower CMAS resistance

SiO_2

CMAS region